Tetrahedron Letters No. 49, pp 4865 - 4868.
0040-4039/78/1201-4865$02.00/0

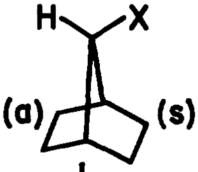
EFFECT OF HALOGEN SUBSTITUENTS ON NMR CHEMICAL SHIFTS. ^{13}C SPECTRA OF BICYCLIC HALIDES.[1]

Kenneth B. Wiberg and William E. Pratt
Department of Chemistry, Yale University, New Haven, Conn. 06520

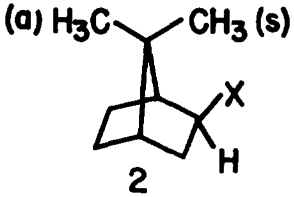
William F. Bailey
Department of Chemistry, University of Connecticut, Storrs, Conn.06268

The question of the relative importance of through-bond and through-space interactions in determining ^{13}C nmr chemical shifts, as well as the relative importance of electric field effects and induced magnetic fields are still not answered. We have examined the ^{13}C nmr spectra of a number of sets (F,Cl,Br,I) of bicyclic halides as well as other aliphatic and alicyclic halides. Some of our results appear to be relevant to the above questions.

The spectra of the 7-halonorbornanes (1) and the 7,7-dimethyl-2-halonorbornanes (2) are of particular interest. The chemical shifts of the carbons indicated by s and a are



1



2

given in Table I. The chemical shifts are with respect to the corresponding carbons in the parent hydrocarbons and thus will be referred to as differential chemical shifts (Δδ). It may first be noted that the chemical shifts of the syn-methyl group in 2 change little on going from Cl to I. Thus, in this case, "steric compression"[2] cannot be of importance.[3] The distance between the halogen and the hydrogens of the C-H bonds is small enough that a large upfield shift would have been expected for the syn-methyl group if steric compression were operative.

Table I[4]

^{13}C Nmr Differential Chemical Shifts (ppm)[a]

Compound	Position	F	Cl	Br	I
1	s	-3.35	-3.15	-2.60	-1.58
1	a	-4.68	-2.52	-2.53	-2.96
2	s,a[b]	-	0.89	0.94	1.18
		-	0.83	0.84	0.86
3	δ[C(4)]	0.07	-0.93	-1.52	-2.72

a. Negative values indicate upfield shifts from the parent hydrocarbon.

b. It has not proved possible to assign chemical shifts to the individual methyl groups in 2.

In 1, the geometry is such that a field effect would be expected to give a large difference in chemical shift between the s and a carbons. The field effect is usually expressed using Buckingham's equation[5] which includes two terms, an electric field squared term $< E^2 >$ and a first power term, E_z. The former drops off as r^{-6} and would be expected to be insignificant past the β-carbon.

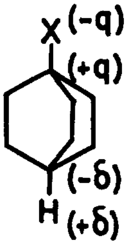
The electric field term for the δ-position of cyclohexyl halides was obtained by Schneider and Freitag[6] by approximating the C-X bond as a dipole with the appropriate charges (q) localized on the two atoms, and then calculating the charges (ΔQ) induced at the carbon in question by the interaction of the charges with each of the C-C and C-H bonds attached to the carbon and summing these quantities.

$$\Delta Q = \frac{\alpha q}{\ell r^2} \cos \theta$$

Here α is the polarizability of the bond, ℓ is the bond length, r is the distance between the charge (q) and the center of the bond, and θ is the angle between the line defining r and the bond. When the ratio of induced charges, $\Sigma\Delta Q_s/\Sigma\Delta Q_a$, is calculated, the C-X bond charges cancel and the ratio depends only on the polarizabilities and the geometry.[7] The calculated $\Sigma\Delta Q$'s predict a relatively large downfield shift at the s position, and a small upfield shift at the a position. For 1 (X=Cl), the ratio of the $\Sigma\Delta Q$'s is -11 whereas the observed ratio of chemical shifts (X=Cl) is +1.3. Neither the sign nor the magnitude are calculated correctly.

Schneider and Freitag recognized the difficulty with the γ-position in cyclohexyl halides and suggested the addition of a small charge at the β-position caused by charge alternation.[6] If such a charge were present, it would lead to an upfield shift for both carbons. Their suggestion of a 2% charge shift leads to a reduction of the calculated ratio but not a change in sign. No reasonable variant of the field effect appears capable of explaining the upfield shifts found at position s in compound 1 (X=F, Cl, Br, I). Moreover, the change in relative shifts for the s and a carbons of 1 as the halogen is varied is not explained by this model.

Their treatment was particularly successful with the δ-position of cyclohexyl halides.[6] The C(4) carbon of 1-halobicyclo[2.2.2]octanes (3)[8] provide another case in which the δ-position can be examined.



3

The C-X dipole will have a minor interaction with the C_3-C_4 bonds since the angle between the distance vector and the bond vector is near 90°.[9] The interaction with the C(4)-H bond will predominate and create a small negative charge at the 4-carbon. Thus the field predicts an upfield shift which decreases on going from F to I due to the decrease in the magnitude of q. The differential chemical shifts are: F, 0.07; Cl, -0.93; Br, -1.52 and I, -2.71. The observed shifts move upfield on going from F to I, in the opposite direction from that expected from a field effect. We conclude that the field effect is not a major contributor to γ and δ

^{13}C chemical shifts.

The range of chemical shifts for the α-positions of compound 3 (F→I) is 46.7 ppm, and that at the δ-position is 2.79 ppm,[8] a ratio of 17:1. The upfield shift at the α-position on going from the fluoride to the iodide can only be due to an induced magnetic field caused by circulation of the electrons of the halogen. Since the 4-carbon is co-linear with the C-X bond, the effect of this field should drop off as r^{-3}.[10] The ratio of the distance from the halogen to the 4- and 1-carbons raised to the third power is 13:1. The agreement between these ratios suggest that induced magnetic fields are of importance even at locations as remote as the δ-position.

This conclusion concerning the δ-position is reinforced by the results of a factor analysis study[11] of the ^{13}C chemical shifts (Table II). The b_2 terms, which correspond to slopes of plots of chemical shifts against halogen parameters, are of particular interest in this context. With 3 where the carbon in question lies on the C-X axis, b_2 has the largest negative value. As the carbon is moved away from this axis as in the cyclohexyl halides, b_2 approximates zero. Finally, with the δ-positions of the 2-norbornyl halides, which have the largest displacement from the C-X axis, b_2 becomes positive.

The γ-positions present a more complex situation in which through-bond, magnetic anisotropy, and possibly other effects cooperate togive the observed chemical shifts. These cases will be considered in detail at a later time.

Table II

Results of Factor Analysis for δ-Positions

Molecule	b_1	b_2	b_3	rms error (ppm)
Cyclohexyl	-1.18	-0.03	0.09	0.01
2-Norbornyl	-2.36	0.24	0.15	0.14
1-Bicyclo[2.2.2]octyl	1.02	-0.91	-0.05	0.01
1-Bicyclo[3.3.1]nonyl	-1.67	-0.30	0.47	0.03
1-Adamantyl	-1.79	-0.10	0.20	0.01
2-Adamantyl (syn)	-1.57	0.07	0.17	0.04
2-Adamantyl (anti)	-1.22	0.15	0.07	0.01

References

1. This investigation was supported by grant CHE 7419380 from the National Science Foundation. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

2. D.M. Grant and B.V. Cheney, J.Am.Chem.Soc., **89**, 5315 (1967).

3. If the large upfield shift expected for the syn-methyl group of 2 due to steric compression on going from Cl to I as the substituent were cancelled by some other factor which changed with substituent, a change in chemical shift would be expected for the anti-methyl group. Since the chemical shifts for the two methyl groups are essentially unchanged through the series, a cancellation of effects seems unlikely. For other examples where steric compression does not appear to be of importance, see: A.J. Jones, P.D. Gardner, D.M. Grant, W.M. Litchman and V. Boekelheide, J.Am.Chem.Soc., **92**, 2386 (1970); J.B. Stothers and C.T. Tan, Can.J.Chem., **54**, 917 (1976);

H.-J. Schneider and E.F. Weigand, *J.Am.Chem.Soc.*, **99**, 8362 (1977).

4. The assignment of s and a carbons in 1, X=Cl, was made by recording the spectrum of *exo*, *exo*-2,3-dideuterio-*syn*-7-chloronorbornane [R.G. Weiss and E.I. Snyder, *J.Org.Chem.*, **35**, 1627 (1970)]. The assignments for 7-fluoro- and 7-iodonorbornane was made by selective proton decoupling experiments which will be described in detail elsewhere. The s and a carbons of 7-bromonorbornane are almost degenerate and the assignments are tentative. It has not proved possible to assign chemical shifts to the individual methyl groups in 2 since they too are almost degenerate.

5. W.T. Raynes, A.D. Buckingham and H.J. Berstein, *J.Chem.Phys.*, **36**, 3481 (1962).

6. H.-J. Schneider and W. Greitag, *J.Am.Chem.Soc.*, **99**, 8363 (1977).

7. The geometry used was that of norbornane: J.F. Chiang, C.F. Wilcox, Jr., and S.H. Bauer, *J.Am.Chem.Soc.*, **90**, 3149 (1968).

8. The ^{13}C chemical shifts of the 1-halobicyclo[2 2,2]octanes (F,Br,Cl) have been reported by G.E. Maciel and H.C. Dorn, *J.Am.Chem.Soc.*, **93**, 1268 (1971). The values cited herein were obtained in the present investigation.

9. The geometry was assumed to be independent of halogen substitution, and was taken from E. Hirota, *J.Mol.Spectrosc.*, **38**, 367 (1971).

10. H.M. McConnell, *J.Chem.Phys.*, **27**, 226 (1957).

11. K.B. Wiberg, W.E. Pratt and W.F. Bailey, preceding paper.

(Received in USA 25 August 1978)