not be obtained by fractional distillation, as evidenced by the somewhat low N value, the correspondingly high titration equivalent, and the presence of a small amount of carbonyl absorption at 1720 cm.$^{-1}$ (see Fig. 1).

The experiments with the other carbonyl compounds, mentioned in this paper, were carried out essentially in the same manner as described in the four examples given above. Titration equivalents were determined by neutralization with 0.1 N HCl in aqueous medium, using methyl orange as the indicator. The infrared spectra were measured in chloroform solution (usually about 10%) on a Perkin-Elmer model 12C or a Baird double beam spectrophotometer.

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Shifts in Nuclear Magnetic Resonance Absorption Due to Steric Effects. II. Polysubstituted Cyclohexanes

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The ring protons in a polysubstituted cyclohexane are shifted toward lower field when they are adjacent to a more bulky substituent. The extent of the shift is proportional to the number and proximity of the substituents. For hexasubstituted cyclohexanes of identical stereochemistry the spectra are the same if the substituent is chlorine or hydroxyl.

Introduction

The stereochemistry of most isomers of the inositols, the hexachloro- and the heptachlorocyclohexanes have been established.[1,2] Therefore the arrangement of substituents with respect to the ring protons is known. When the ring interconverts from one chair conformation to another, protons which were in an equatorial position become axial and *vice versa.* However, this interconversion will only occur to an appreciable extent if both conformations have the same number of substituents opposing each other in axial positions, since otherwise there is an appreciable energy difference between the two forms. Isomers having three axial substituents might be expected to interconvert readily.[3] If this interconversion is rapid the magnetic environment of the ring protons, as observed by proton magnetic resonance spectroscopy, would be the average of that in the two conformations.[4] For those isomers which do not contain three axial substituents the ring protons will be in a constant environment.

Inductive effects on the bonding electrons of all the ring protons will be identical in 1,2,3,4,5,6-hexasubstituted cyclohexanes since the protons are attached to carbon atoms which are similarly substituted. Any departure of the proton resonance spectra from a single sharp peak will therefore be due to long range magnetic shielding effects. In principle this shielding is calculable from magnetic anisotropies but would be very difficult to determine.[5] The change in magnetic shielding is empirically correlated with the proximity of substituents and will therefore be treated as a steric effect although the actual mechanism of the shielding may arise from another cause. The interpretation of the spectra in terms of steric effects are done with this reservation. Except for a constant displacement, the spectra of equivalent stereoisomers should be identical provided the size of the different substituents is similar.

Experimental

The proton magnetic resonance spectra were obtained as previously described.[6] Saturated methylene chloride solutions of the hexa- and heptachlorocyclohexanes were used and the peak due to the solvent protons was used as an internal standard. Since the solvent is chemically similar to the solute, no account was taken of possible chemical shifts due to concentration effects or association.[7] Saturated carbon tetrachloride solutions of the heptachlorocyclohexanes were also used since some of the isomers absorbed at a similar field to the protons of the methylene chloride.

The hydroxyl hydrogens of the inositols were twice exchanged with a tenfold excess of 99% deuterium oxide and the spectra obtained in deuterium oxide as solvent. The concentrations were either 1.8 molar or saturated, whichever was more dilute. Methylene chloride was used as an external standard in an annular cell.[8]

The separation between the absorption due to the residual protons in the deuterium oxide and the protons of the external standard was the same for every sample. This was taken as an indication that any changes in concentration between these samples did not affect the chemical shift.

Results

Table I lists the results which were obtained. To facilitate comparison the chemical shift due to a difference in substituents, which is 34 cycles, has been subtracted from the observed values for the inositols, and the modified values listed in the third column of the table. The corresponding stereoisomers of the inositols and hexachlorocyclohexanes are listed in the same row. The details of the spectra for the γ- and ϵ-isomers of heptachlorocyclohexane are shown in Fig. 1, and that for *epi*-inositol in Fig. 2. The spectra were obtained at 40 Mc. and the observed shift is in cycles/sec. toward higher field from the signal due to the protons in methylene chloride. The spectra of the hexa-

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(1) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).

(2) S. J. Angyal, *Quart. Revs.*, **11**, 212 (1957).

(3) H. D. Orloff, *et al.*, THIS JOURNAL, **75**, 4243 (1953).

(4) H. J. Bernstein, Abstracts of Papers at September, 1957, A.C.S. Meeting 11-S.

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

(6) S. Brownstein, THIS JOURNAL, **80**, 2300 (1958).

(7) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(8) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

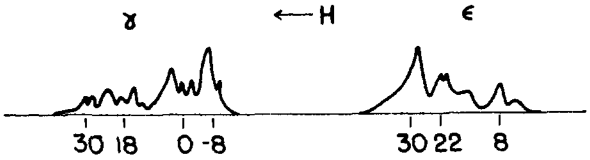

Fig. 1.

chlorocyclohexanes agree within experimental error with those obtained by Bernstein in dioxane solution.[9]

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF POLYSUBSTITUTED CYCLOHEXANES

Hexasubstd. -Cl substd.		-OD substd.		-OD-34 cycles
α	23 (2)	L	63 (2)	29
	39 (1)		79 (1)	45
β	52	*scyllo*	82	48
γ	25	*muco*	61	27
δ	47	*myo*	75	41
	26		55	21
ε	32 (2)	*neo*[a]	47	13
	25 (1)			
θ		*epi*	71	37
			69	35
			56	22
i		*cis*	61	27
η		*allo*	55	21

Heptachlorocyclohexanes

α—39
26
γ—20
0
δ—15
ε—30
22
8

[a] This value is uncertain since the solution was hot and dilute and the signal very weak.

Discussion

Steric effects on proton magnetic resonance spectra have been observed in aromatic compounds,[5,10a] and for the protons in cyclic aliphatic compounds.[10,11,12] In an aliphatic system close proximity to a bulky group might cause a shift to lower field due to a second-order paramagnetic effect.[13] This has been observed by Lemieux,[10b] and postulated by Tiers for fluorine magnetic resonance.[14]

The α-isomer of hexachlorocyclohexane and the D- and L-isomers of inositol have four axial hydrogens, each pair of which adjoins an axial substituent, and two equatorial hydrogens. A molecular model constructed to scale shows the equatorial hydrogens to be partly surrounded by substituents but not too crowded.[15] Therefore one can attribute the peak observed at higher field to the equatorial hydrogens and that at lower field to the axial hydrogens. The relative intensities of the two peaks, approximately 1:2, agree with this assignment. Fine structure which is observed for the α-isomer may be explained by spin–spin coupling. The fine structure was not resolvable for L-inositol.

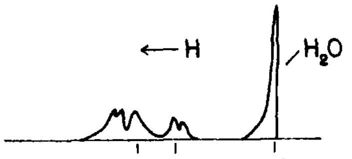

Fig. 2.

β-Hexachlorocyclohexane and *scyllo*-inositol have six axial hydrogens and therefore only show a single peak. Only a single peak is observed for γ-hexachlorocyclohexane and *muco*-inositol although they have both axial and equatorial hydrogens attached to the cyclohexane rings. This is presumed to be due to the rapid interconversion of one chair form to the other, in which the position of the hydrogens is reversed. Only the average environment of the hydrogens, which is identical for all, is observed.

In the δ- and *myo*-isomers there are two axial hydrogens adjacent to an axial substituent, and three axial hydrogens not adjacent to a substituent. There is also one equatorial hydrogen largely surrounded by substituents. The peak at higher field is assigned to the axial hydrogens, and the one at lower field to the equatorial hydrogen. For these isomers there is a discrepancy with the other results since it would be expected that not all the axial hydrogens would show resonance at the same field strength.

ε-Hexachlorocyclohexane and *neo*-inositol have four axial hydrogens, each pair of which is adjacent to an axial substituent. There are also two equatorial hydrogens which are largely surrounded by substituents. Two peaks were observed for the epsilon isomer, with relative intensities of 2:1. The *neo*-isomer was quite insoluble and only a single weak signal was observed in a hot solution. Any less intense signals would be hidden in the noise.

epi-Inositol has three axial hydrogens not adjacent to bulky substituents and one axial hydrogen adjacent to two substituents. It also has two equatorial hydrogens partly surrounded by substituents. Three peaks are observed as shown in Fig. 2 and the relative intensities support an assignment on the above basis. In *cis*-inositol and *allo*-inositol there are three axial hydrogens and three equatorial hydrogens. However, ring interconversion yields an equivalent molecule in which the hydrogens are interchanged, so only a single line is observed.

The situation is more complicated with the heptachlorocyclohexanes since differences in inductive effects may occur. The spectra obtained for the α- and ε-isomers agree with a strictly steric interpretation and that of the γ-isomer neither confirms nor denies such a treatment. The spectrum for the δ-isomer cannot be explained by steric effects alone nor in a very satisfactory manner when inductive effects are included.

α-Heptachlorocyclohexane has three axial hydrogens not adjacent to an axial chlorine and two axial hydrogens adjacent to one axial chlorine. Therefore in the spectrum two peaks of not too dif-

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(9) R. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, THIS JOURNAL, **80**, 6098 (1958).

(10) (a) C. Reid, *J. Molec. Spectroscopy*, **1**, 18 (1957); (b) R. U. Lemieux, *et al.*, THIS JOURNAL, **79**, 1005 (1957).

(11) W. D. Kumler, J. N. Shoolery and F. V. Brutcher, *ibid.*, **80**, 2533 (1958).

(12) R. U. Lemieux, R. K. Kullnig and R. Y. Moir, *ibid.*, **80**, 2237 (1958).

(13) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

(14) G. V. D. Tiers, THIS JOURNAL, **78**, 2914 (1956).

(15) H. A. Stuart, *Z. physik. Chem.*, **B27**, 350 (1934); models supplied, Waltham Abbey, Essex, Eng.

ferent intensity are observed with the more intense at higher field. ϵ-Heptachlorocyclohexane has two axial hydrogens adjacent to an axial chlorine, one axial hydrogen adjacent to two axial chlorines and two equatorial hydrogens highly surrounded by chlorine. Its spectrum shown in Fig. 1 fits the steric interpretation.

In the γ-isomer, which contains four axial hydrogens each pair of which adjoins an axial chlorine and one equatorial hydrogen highly surrounded by chlorine, a complex spectrum is obtained. This seems to be due to an interaction between chemical shift and spin–spin coupling and the peaks cannot be assigned with certainty.[16]

The δ-isomer has two axial hydrogens adjacent to one axial chlorine, one axial hydrogen adjacent to two axial chlorines, and two equatorial hydrogens partly surrounded by chlorines. If the ring converts to its other conformation the equatorial hydrogens become axial and adjacent to two axial chlorines, while the hydrogen in this environment previously becomes equatorial. However, the two axial hydrogens adjacent to one axial chlorine become equatorial and largely surrounded by chlorine. The carbon atoms attached to these hydrogens adjoin the disubstituted ring carbon atom which might cause a chemical shift to lower field because of an inductive effect. If the inductive effect and rapid ring interconversion occur, a single proton resonance peak might be expected. Without the inductive effect ring interconversion would still give rise to two peaks since the conformations are not equivalent. However, only a single peak was found.

After a correction for chemical shift it is found that ring protons in a similar environment have their resonance absorption in the same region. This is shown in Table II. The axial hydrogens adjacent to one substituent in the δ- and *myo*-isomer are the only discrepancy.

TABLE II

STERIC EFFECT ON RING PROTON ABSORPTION

Axial hydrogen alone	52 (β 6)	37 epi	39 (α 7)
	47 (δ 6)	48-*scyllo*	
		41 *myo*	
Axial hydrogens with 1 axial substituent	23 (α 6)	29-L	26 (a 7)
	47 (δ 6)	41-*myo*	20 (γ 7)[b]
	32 (ϵ 6)	13 *neo*[a]	30 (ϵ 7)
Axial hydrogen with 2 axial substituents		22-*epi*	8 (ϵ 7)
Equat. hydrogen largely surrounded by subst.	26 (δ 6)	21-*myo*	0 (γ 7)[b]
	25 (ϵ 6)		22 (ϵ 7)
Equat. hydrogen partly surrounded by subst.	39 (α 6)	45-L	
		35-*epi*	

[a] Doubtful due to weak signal and hot solution. [b] Only approximate because of chemical shift spin–spin interaction.

Conclusion.—In hexasubstituted cyclohexanes where the inductive effect is the same for all the ring protons several absorption peaks may be observed. These can be correlated with the proximity of substituents which shift the resonance of the more sterically hindered protons to a lower field. A similar effect is observed in the proton resonance spectra of the heptachlorocyclohexanes.

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ITHACA, N. Y.

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[16] H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

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Resonance Energies of Conjugated Acetylenes

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Inductive and resonance effects on the heats of hydrogenation of substituted acetylenes have been evaluated. Inductive effects are about twice as large as those in olefin hydrogenation, and the Baker–Nathan effect per α-hydrogen is about half again as large, but resonance effects due to conjugation are slightly smaller. Resonance effects due to conjugation are a function of the dimensions of the π-bond system but, to a good approximation, independent of the nature of the atoms involved. All this is in good accord with the predictions of simple L.C.A.O.–M.O. theory.

Flitcroft and Skinner recently have measured the heats of hydrogenation of a number of substituted acetylenes.[1,2] They observed that for all compounds containing the structural feature $-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{COX}$, the heat of hydrogenation was *higher* (*i.e.*, *more* heat was given off) than for the corresponding unsubstituted acetylene.[1] They correctly concluded that inductive effects (ionic–covalent resonance) were responsible for this apparent anomaly. The present paper shows that a set of resonance energies for conjugated acetylenes which are all of the proper sign and of a reasonable magnitude can be obtained if inductive and resonance effects are assumed to be additive and inductive and Baker–Nathan effects are quantitatively accounted for. (In this paper the experimentally observed stabilization of a molecule containing one or more hydrogen atoms alpha to a π-electron system will be called the Baker–Nathan effect.)

Unconjugated Acetylenes.—Taft and Kreevoy[3] have suggested that the heats of hydrogenation of non-conjugated acetylenes to saturated hydro-

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[1] T. L. Flitcroft and H. A. Skinner, *Transactions of the Faraday Society*, **54**, 47 (1958).

[2] T. L. Flitcroft, H. A. Skinner and M. C. Whiting, *ibid.*, **53**, 784 (1957).

[3] R. W. Taft, Jr., and M. M. Kreevoy, THIS JOURNAL, **79**, 4011 (1957).