Nuclear Magnetic Shielding of Hydrogen in the Hydrides of the Elements

By **Joan Mason**, Open University, Milton Keynes MK7 6AA

Values have been assembled for the molecular diamagnetic and paramagnetic components of the proton shielding in the simple binary hydrides of the elements, and are shown to increase in periodic fashion with the atomic number of the heavy atom. For molecules for which the diamagnetic term σ_d is unknown, this has been calculated by Flygare's method. An absolute value of the paramagnetic term is afforded by the spin-rotation interaction constants which are now known with reasonable accuracy for 13 of the hydrides (σ_p has been calculated where necessary from Ramsey and Flygare's equations). For the remaining hydrides, σ_p has been obtained by subtracting σ_d from the observed shielding referred to an absolute scale. The dependence of the terms on the size and shape of the molecule and the position of the hydrogen is illustrated by the values for diborane and tetrahydroborate ion. Factors determining the periodicity are discussed; this is remarkably symmetrical for the diamagnetic and paramagnetic terms. Although proton shielding is often described as dominated by the diamagnetic term, the periodic correlation shows that variations in the resultant shielding may be determined by changes in the paramagnetic term, *e.g.* down the Group of the heavy atom and across the second Row (the lithium Row).

IN the quarter-century since Ramsey's description[1] of nuclear magnetic screening as the resultant of two molecular terms, diamagnetic (σ_d) and paramagnetic (σ_p), there have been many attempts to calculate σ_p, but this is very difficult for molecules more complicated than

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[1] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.

hydrogen because of our lack of knowledge of wavefunctions of excited states. Expressing [2] the shielding as a sum of atomic contributions, σ_d^A and σ_p^A, plus the contributions σ^{AB} from electronic circulations on other atoms B, has provided shielding terms that are more meaningful for the chemist, but σ_p^A and σ^{AB} cannot be observed directly and are difficult to calculate, particularly for protons for which σ^{AB} is peculiarly important. Simple interpretations in terms of inductive effects, for example, may run into anomalies which arise from terms neglected or underestimated in this division of the shielding.

In the meantime, however, there has been an accumulation in the literature of molecular beam [3] and microwave spectroscopy [4] of spin-rotation interaction (magmetic hyperfine-structure) constants C_i from which an absolute and reasonably accurate value of Ramsey's molecular paramagnetic term, σ_p, can be obtained. When a molecule rotates the circulation of the valence electrons produces magnetic fields at a nucleus which have the same dependence on the electronic structure of the molecule as does the induced field in conventional n.m.r. experiments, which reinforces the applied field but is opposed by the Lamb term. Relations between C_i and σ_p have been given by Ramsey [1,3,5] for linear molecules and by Flygare [6] for symmetric- and asymmetric-top molecules. Flygare has also given useful approximations for the calculation of the diamagnetic term.[7] As Flygare has pointed out, this forms the link between the relative shielding, δ, measured in conventional n.m.r. experiments, and the absolute shielding σ. The shielding constants are in the form given also by theory, *i.e.* for the gaseous molecule relative to the bare nucleus.*

The limitation to simple molecules for which the hyperfine structure can be seen suits the present purpose, which is to see how the periodicity in the absolute shielding of the proton in binary hydrides of the elements can contribute to the chemical understanding of nuclear magnetic shielding.

RESULTS AND DISCUSSION

The Table contains the values of the proton-shielding terms that are plotted in Figure 1 against the atomic number of the heavy atom in the hydride. The values of σ_d, plotted as closed squares in the Figures, are all-atom values calculated according to the Ramsey definition.[1] Values are available for H_2,[8] LiH,[9a] B_2H_6,[10] and HF,[9] for CH_4, NH_3, and H_2O,[11] and for SiH_4, PH_3, H_2S, and HCl.[12] For the other hydrides σ_d values have been obtained by Flygare's method [7] with bond lengths from the Chemical Society's Tables [13a] or from the literature (*e.g.* for $[ReH_9]^{2-}$ and $[TcH_9]^{2-}$; [13b] σ_d is 17.75 p.p.m. for the free hydrogen atom, 24.38 p.p.m. for the gaseous hydride ion.[14] σ_d Values calculated by Flygare's method agreed within *ca.* 1 p.p.m. with values from *ab initio* calculations when available. (Differences in reported values may be due to the use of slightly different molecular geometries.)

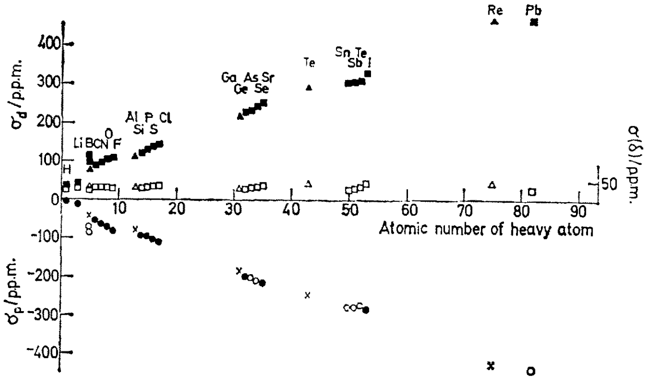

FIGURE 1 Absolute shielding parameters for the proton in the simple binary hydrides of the elements, plotted against the atomic number of the central atom: σ_d(calc.) for hydride molecules (■) and ions (▲); $\sigma(\delta)$ for hydride molecules (□) and ions (△); σ_p(obs.) (●); $\sigma_p(\delta)$ for hydride molecules (○) and ions (×)

Values of σ_p(obs.), plotted as closed circles, were obtained from values of the spin-rotation coupling constant at the hydrogen nucleus, C_i^H, determined by molecular-beam magnetic resonance for H_2,[15] HD,[16] CH_4,[17] SiH_4 and GeH_4,[18] HF,[19] HCl,[20] and HBr and HI,[5a] by molecular-beam electric resonance for LiH,[21]

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* Following recommended sign conventions (I.U.P.A.C., 1972), δ (relative to $SiMe_4$) is considered to be positive downfield, although the absolute screening, σ, is positive upfield. Ramsey's sign convention for C_i is followed as given by the Hamiltonian $\mathscr{H} = -hC_i\, \boldsymbol{I}.\boldsymbol{J}$ (most microwave spectroscopists define C_i with the opposite sign).

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Absolute values of the nuclear magnetic shielding parameters for the proton in the hydrides of the elements. Numbers in parentheses are uncertainties (in units of the last digit) as given by the original authors. The derivation of the shielding constants is explained in the text

Molecule	σ_d (calc.) p.p.m.	Ref.	C_I^H kHz	Ref.	σ_p (obs.) p.p.m.	σ_T p.p.m.	δ[a] p.p.m.	Ref.	$\sigma(\delta)$ p.p.m.	$\sigma_p(\delta)$ p.p.m.
H_2	32.0	8	113.90(3)	3, 15	−5.8	26.17	4.06		26.2	−5.8
HD			85.60 (2)	16	−5.65 (8)					
LiH	39.5	9*a*	8(1)	21	−13·8 (5)	25.7				
$[BH_4]^-$	75.7						−2.0 (aq)	*b*	33.8	−41.9
B_2H_6 (bridge)	111.5	10					−0.53 (15 atm)	*c*	31.2	−80.3
(terminal)	97.0						3.95 (15 atm)		26.7	−70.3
CH_4	87.2	11	C_a 10.4 (1), C_d 18.5 (5)	17, 22	−56.4	30.8	−0.24 (g)		30.52	−56.7
NH_3	96.0	11	C_x 1.62, C_y 16.11, C_z 18.94	29	−65.3	30.8	−0.31 (g)	*d*	30.6	−65.4
H_2O	102.8	11	32.70 (20)	27, 28	−71.8	31.0	0.31 (5 atm)	*e*, 33	29.96	−72.8
HF	108.4	9	70.6 (1.3)	26	−79.7 (3)	28.7	1.85 (g)	34	28.4	−80.0
$[AlH_4]^-$	106						0.0 (soln.)	*f*	31.8	−74
SiH_4	120.5	12	C_a 3.88 (23), C_d 9.0 (3.5)	18	−95	25.5	2.75 (10 atm)	*g*	27.5	−93
PH_3	127.6	12	C_α 3.01 (8), C_β 7.69 (19)	23	−98.1	29.5	1.21 (12 atm)	*g*	29.1	−98.5
H_2S	136.1	12	16.239 (10)	24, 30	−104	32.1	−0.17 (g)	*h*	30.4	−105.7
HCl	141.9	12	41.70 (10) for $H^{35}Cl$	20, 25	−110.9	32.4	−0.73 (g)	*h*	31.0	−110.9
$[GaH_4]^-$	206.1						0.5 (soln.)	*i*	31.3	−175
GeH_4	226		C_a 3.62 (20), C_d 5.5 (5.0)	18	−201	25	2.60 (? atm)	*j*	27.7	−198
AsH_3	230						1.47 (CCl_4)	*k*	30.2	−200
H_2Se	241						−2.31 (g)	*e*	32.6	−208
HBr	251		43 (3)	5*a*	−214	37	−4.58 (g)	*d*	34.9	−216
$[TcH_9]^{2-}$	288						−9.5 (aq)	13	39.8	−248
SnH_4	304						3.87 (CCl_4)	*l*, *m*	27.8	−276
SbH_3	306						1.38 (CCl_4)	*k*	30.3	−276
H_2Te	311						−7.08 (1 atm)	*e*	37.4	−274
HI	329		49.7 (1.0)	5*a*	−283	46	−13.49 (20 atm)	*g*	43.8	−285
$[ReH_9]^{2-}$	466						−10.2 (aq)	*n*	40.5	−426
PbH_4	465						6.8 (soln.)	*o*	24.9	−440
H^- (g)						27.38		14		
H (atom) (g)						17.73		32		
H^+ (g)						0.0				

[a] Values labelled (g) are for the gas with extrapolation to zero pressure. For gases measured under pressure the δ values are followed by the pressure in parentheses. All δ values measured in CCl_4 solution were extrapolated to infinite dilution, and all $\sigma(\delta)$ values obtained from liquids were corrected for bulk susceptibility. [b] R. A. Ogg, *J. Chem. Phys.*, 1954, **22**, 1933. [c] D. F. Gaines, R. Schaeffer, and F. Tebbe, *J. Phys. Chem.*, 1963, **67**, 1937. [d] G. Widenlocher, *Ann. Phys.*, 1966, 327. [e] J. C. Hindman, A. Svirmickas, and W. B. Dixon, *J. Chem. Phys.*, 1967, **47**, 4658. [f] Estimated from the value for $Me_3N{\cdot}Al\mathit{H}_3$ given by N. N. Greenwood, E. J. F. Ross, and A. Storr, *J. Chem. Soc.*, 1965, 1400. [g] W. G. Schneider, J. A. Pople, and H. J. Bernstein, *J. Chem. Phys.*, 1958, **28**, 601. [h] W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, 1962, **36**, 3481. [i] Estimated from the value for $Me_3N{\cdot}Ga\mathit{H}_3$ in *f*. [j] K. M. MacKay, quoted by E. A. V. Ebsworth in 'Volatile Compounds of Silicon,' Pergamon, 1963, p. 16. [k] E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1967, **63**, 1071. [l] P. E. Potter, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1964, 524. [m] N. Flitcroft and H. G. Kaesz, *J. Amer. Chem. Soc.*, 1963, **85**, 1377. [n] A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Amer. Chem. Soc.*, 1961, **83**, 4909. [o] Estimated from values for $Me_3Pb\mathit{H}$, $Me_3Sn\mathit{H}$, and SnH_4 in *m*.

CH_4,[22] PH_3,[23] H_2S,[24] and HCl,[25] and by microwave spectroscopy for HF,[26] H_2O,[27,28] NH_3,[29] and H_2S,[30] the last three by molecular-beam maser.[28-30] Vibrational effects were neglected in the calculation of σ_p from C_i.

The value for the absolute shielding σ, plotted in the Figures as open squares, is $\sigma(\delta)$ obtained from conventional n.m.r. spectroscopy by referring the chemical shift δ, measured relative to CH_4 gas or to $SiMe_4$, to an absolute scale. δ Values for the gas extrapolated to zero pressure were used as far as possible, and these are available for the lighter molecules for which gas–liquid shifts are large. For the heavier molecules, for which only solution values are available, correction was made for the diamagnetic susceptibility of the liquid in the conversion of δ into σ (δ). The absolute scale is based on Raynes's combination [31] of a precise value [32] for the proton shielding in water with Hindman's relation [33] between this and σ (H_2O, gas) and also σ (CH_4, gas), which Hindermann and Cornwell [34] have related to σ (H_2, gas) in agreement with the molecular-beam results.[15,16] Hydride shifts measured relative to $SiMe_4$ were linked to the absolute scale by Raynes and Raza's measurements [35] which place the proton resonance in $SiMe_4$ (g) as 0.132 p.p.m. upfield of CH_4(g), and in $SiMe_4$ at infinite dilution in CCl_4 as 0.245 p.p.m. downfield of CH_4(g), after correction for bulk susceptibility. The

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scale thus centres on σ (CH_4, gas), to which all the other absolute values of the shielding are related.

For molecules for which σ_p has been measured directly by the spin-rotation interaction the Table gives also σ_T, the absolute shielding obtained by adding σ_p (obs.) to the calculated σ_d. In most cases this agrees within 1 or 2 p.p.m. with the absolute shielding obtained from the chemical shift. Where the agreement is less good, as for SiH_4 and GeH_4, this is because the uncertainty in the spin-rotation constants is relatively large. It seems reasonable then to estimate the paramagnetic term for the hydrides for which no accurate spin-rotation value is available by subtracting the calculated diamagnetic term from $\sigma(\delta)$. The resulting values are labelled $\sigma_p(\delta)$ in the Table and are plotted as open circles in the Figures.

The boron–hydrogen shieldings demonstrate the effects of molecular size and shape, as compared with bond type, on the proton shielding for the same central atom. The values of σ_d and σ_p increase with enlargement of the molecule (as for C_2H_6 compared with CH_4) and $[BH_4]^-$ is seen to fit the periodic correlation, as do $[AlH_4]^-$ and $[GaH_4]^-$, and the nonahydride ions of technetium and rhenium (d^0). The order of the observed shieldings for the bridge and terminal hydrogen atoms in B_2H_6 and the hydridic hydrogen in $[BH_4]^-$ does not match ' chemical ' expectation, since the electron-deficient bridge proton is not the least shielded although the electron-rich proton in $[BH_4]^-$ is the most shielded. These shifts are the result of an increase in σ_d in the order $[BH_4]^- < BH_2 <$ BHB of increasing proximity of the proton to the electrons on two borons, opposed by an increase in $|\sigma_p|$ in the same order (this is also the order of lowering of excited states, and the formation of two weaker bonds instead of one stronger bond at hydrogen). The relative shielding of the bridge and terminal protons in B_2H_6 is ' determined ' by the diamagnetic term, but the proton in $[BH_4]^-$ is the most shielded because the paramagnetic term is small.

The Figures show that the periodicity in the proton shielding is remarkably similar for σ_d and σ_p. The average diamagnetic shielding depends on $\langle\psi_0|r^{-1}|\psi_0\rangle$ summed over all electrons in the molecule, where ψ_0 is the ground-state wavefunction and r the distance of the electron from the origin which is taken at the nucleus in question. The radius term $\langle r^{-1}\rangle$ tends to increase across the Row and down the Group of the heavy atom in the simple binary hydrides. The number of electrons increases steadily for the heavy atom but there is a small periodic variation with the number of ligand hydrogens. This periodicity is not very evident in the hydride shielding, but the dependence on the number of ligand electrons is clear in the corresponding plot for the fluorides.[36]

The paramagnetic term contains the sum of $\langle\psi_0|Lr^{-3}|\psi_k\rangle\langle\psi_k|L|\psi_0\rangle/\Delta E_k$ over all electrons and over all excited states k, where L is the angular momentum of the electron about the nucleus in question. Since the moment of the electron about the nucleus depends on its distance r, the effective r dependence of σ_p for larger values of r may be nearer $\langle r^{-1}\rangle$ than $\langle r^{-3}\rangle$.[2b] This helps to explain the near cancellation of ' distant ' diamagnetic and paramagnetic contributions to the shielding, and the degree of symmetry evident in the Figures. The excitation energy terms $(\Delta E)^{-1}$ tend to decrease across the Row and increase down the Group of the heavy atom in opposition to the r term.

Figures 1 and 2 illustrate the familiar alternation of properties down the Group, due to irregularities in the Periodic Table. The relatively large increase in atomic number (number of electrons) of the ligand, from the first Row (hydrogen) to the second, leads to a correspondingly large increase in σ_d and $|\sigma_p|$, as does the large increase from the third Row to the post-transition elements of the fourth. But σ_d and $|\sigma_p|$ do not increase at the same rate, and whereas the resultant shielding decreases steadily down Group 4 it increases down the halogen Group. Figure 2 shows that σ_d increases steadily down both Groups with the increase in number of electrons, but for the halogens the increase in $|\sigma_p|$ down the Group is less than the increase in σ_d. The behaviour of the intervening groups is intermediate; the shielding decreases then increases down Group 5, but increases steadily in Group 6 as in 7. Thus the variation in proton shielding down the groups is determined by the smaller increase in $|\sigma_p|$ (compared with σ_d) down the later Groups. This is seen also in the ^{19}F shielding in the hexafluorides of elements of Groups 4—7, in which there is no influence of molecular shape.[36] The irregularities can perhaps be traced to the opposing effects of the r and ΔE terms.

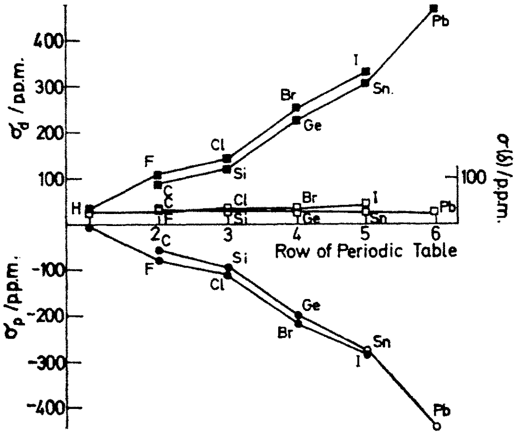

FIGURE 2 Variation in proton-shielding parameters down the Group of the central atom for Groups 4 and 7. The symbols are as in Figure 1

Obviously the resulting shift, seen from the chemist's point of view, depends on a sensitive balance of several factors. The resultant shielding of the proton (in contrast to other nuclei) is always positive and is often described as dominated by the diamagnetic term. But given the steady increase in σ_d with the number of elcetrons in the molecule, we can see important instances in which the variation in the resultant shielding is determined by changes in the paramagnetic term, *e.g.* across

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[36] J. Mason, *J.C.S. Dalton*, following paper.

the second Row and down the Groups. I hope that these correlations will stimulate measurements of proton shielding in metal hydrides, *e.g.* the ionic hydrides of Groups 1 and 2 and diamagnetic hydrides of the transition metals.[37]

I thank Dr. W. T. Raynes for information on the hydrogen shifts.

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