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The Geometry of Nonmetal Hydrides and the Ligand Radius of Hydrogen

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The aim of this paper was to investigate why the geometries of nonmetal hydrides are often not in accordance with the VSEPR model. From a consideration of interligand distances in a variety of BX_4, CX_4, and NX_4 molecules where X is a ligand or a lone pair and in which there are at least two H ligands we have shown that the hydrogen ligands are essentially close-packed. For each of the central atoms we have obtained a value for the ligand radius of hydrogen. These radii decrease with decreasing negative charge and increasing positive charge of the hydrogen ligand as the electronegativity of the central atom increases, as has been found previously for other ligands such as F and Cl. We show that ligand–ligand intractions are an important factor in determining bond angles in hydrides and that the ligand close-packing (LCP) model gives a better explanation of bond angles than the VSEPR model according to which bond angles depend on the electronegativity of the ligand rather than on its size. For example, although the very small angles in PH_3 and SH_2 are not in accord with the VSEPR model, they are consistent with the LCP model in that they are a consequence of the small size of hydrogen ligands which are pushed together by the lone pairs until they are almost close-packed.

Introduction

It was suggested 40 years ago by Bartell that ligand−ligand repulsions are important in determining geometry for many molecules in which carbon is the central atom.[1,2] But for many years this suggestion was not further developed and the VSEPR model became the most commonly used simple model for discussing molecular geometry. However, in the past few years Bartell's proposal has been reexamined and shown to apply not only to molecules in which carbon is the central atom but also to molecules of boron, nitrogen, and oxygen. From an extensive survey of ligand−ligand distances in these molecules it was shown that a characteristic ligand radius can be attributed to the ligands F, Cl, and O and that these radii can be used to rationalize bond angles and interligand distances.[3−7] This work led to the development of the ligand close-packing (LCP) model according to which approximately spherical monatomic ligands are considered to be close-packed around a spherical central atom.[5−7] When there are lone pairs in the valence shell of the central atom, they are considered as pseudo-ligands although they cannot be assigned a lone-pair radius because a lone pair expands to take up any available space in the valence shell, pushing the ligands together until they "touch". More recently we have shown that the six-coordinated fluorides of the period 3 elements, Si, P, S, and Cl, have close-packed ligands from which the fluorine ligand radii can be deduced.[8]

For many molecules the predictions of the LCP model are the same as those of the VSEPR model. Both models emphasize the predominant role played by lone pairs in determining geometry. Although the VSEPR model has enjoyed considerable success, attention has often been drawn to certain exceptions, particularly for molecules in which hydrogen is a ligand. For instance, according to the VSEPR model bond angles decrease with increasing electronegativity of the ligand so that, for example, the bond angle in NF_3 (102.4°) is smaller than that in NH_3 (107.3°), but in contrast the bond angle in PF_3 (97.8°) is larger than the bond angle

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Table 1. BH Bond Lengths, HBH Angles, and H···H Distances for Some Boron Molecules[a]

	B−H	∠H−B−H	H···H	r(H)	ref
BH_3	118.5	120.0	205.2	103	*c*
H_2BNH_2[b]	118.4	121.3	206.4	103	*d*
H_2BBH_2[b]	119.0	116.0	201.8	101	*e*
BH_4^- [b]	123.7	109.5	202.0	101	*f*
H_3BF^- [b]	124.7	108.2	202.0	101	*f*
H_3BCl^-	120.3	113.5	201.2	101	*g*
H_3BCO	122.1	114.5	205.4	103	*h*
H_3BNMe_3	121.1	113.6	202.7	101	*i*
H_3BPH_3	121.2	114.6	204.0	102	*j*
H_3BPMe_3	121.2	113.5	203.0	102	*k*
H_3BPF_3	120.7	115.0	203.7	102	*l*
average				102 ± 1	

[a] Distances in pm and angles in degrees. [b] Ab initio structures. [c] Kawaguchi, K. *J. Chem. Phys.* **1992**, *96*, 3411. [d] Fjeldberg, T.; Gundersen, G.; Jonuik, T.; Saebø, T. *Acta Chem. Scand.* **1980**, *34a*, 547. [e] Mohr, R. R.; Lipscomb, W. N. *Inorg. Chem.* **1986**, *25*, 1053. [f] Frenking, G.; Fau, S.; Marchand, C. M.; Grütmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648. [g] Lawrence, C. H.; Shore, S. G.; Koetzle, T. F.; Huffman, J. C.; Wei, C.-Y.; Bau, R. *Inorg. Chem.* **1985**, *24*, 3171. [h] Venkatachar, A. C.; Taylor, R. C.; Kuczkowski, R. L. *J. Mol. Struct.* **1977**, *38*, 17. [i] Durig, J.; Li, Y. S.; Odom, J. D. *J. Mol. Struct.* **1973**, *16*, 443. [j] Durig, J. R.; Li, Y. S.; Carreira, L. A.; Odom, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 2491. [k] Bryan, P. S.; Kuczkowski, R. L. *Inorg. Chem.* **1972**, *11*, 553. [l] Kuczkowski, R. L.; Lide, D. R. *J. Chem. Phys.* **1967**, *46*, 357.

in PH_3 (93.3°) in contradiction to the prediction of the VSEPR model.

In this paper we show that the apparently anomalous bond angles in some hydrides are, however, consistent with the LCP model, which for these hydrides predicts different bond angles than the VSEPR model. We have determined the ligand radius of hydrogen for the central atoms B, C, N, and O from a survey of the geometric data for molecules of these elements having at least two hydrogen ligands. Some slightly different preliminary values for the ligand radius of hydrogen have been published previously,[5−7] but the values given here, which are based on a larger number of molecules, are more reliable.

Results and Discussion

It is well-known that hydrogen atoms are difficult to locate accurately by X-ray crystallography. Only neutron diffraction for solids and electron diffraction, high resolution Raman and infrared, or microwave spectroscopy for simple molecules in the gas phase can give accurate data for hydrides. Consequently the amount of reliable experimental data for hydrides is somewhat limited and we have, accordingly, made use of data obtained by ab initio and DFT calculations for a few molecules for which experimental data is not available.

The BH bond lengths, HBH bond angles, and H···H distances for a number of simple molecules of boron with two or more BH bonds are given in Table 1. The H···H distances vary only over a small range for both three- and four-coordinated boron so that the H ligands may be regarded as essentially close-packed. The corresponding ligand radius of hydrogen bonded to boron, $r_H(B)$, is almost constant from molecule to molecule and has an average value of 102 pm.

Table 2. CH Bond Lengths, HCH Bond Angles, and H···H Distances for Some Carbon Molecules[a]

	C−H	∠H−C−H	H···H	r(H)	ref
		4-Coordinated			
CH_4	108.4	109.5	176.9	88	*b*
C_2H_6	109.4	107.8	176.8	88	*c*
CH_3F	110.5	109.9	180.9	90	*d*
CH_2F_2	109.2	111.9	181	91	*e*
CH_3Cl	109.6	110.9	180.5	90	*f*
CH_2Cl_2	108.7	111.5	179.8	90	*g*
CH_2ClF	107.8	111.9	178.6	89	*h*
CH_3Br	109.5	111.6	181.2	91	*f*
CH_2Br_2	107.1	110.9	175.4	88	*i*
CH_3I	109.6	111.8	181.2	91	*f*
CH_3CN	110.3	109.4	180	90	*f*
CH_3NC	110.2	109.8	180.3	90	*f*
CH_3NH_2	111.2	108.4	180.4	90	*j*
CH_3OH	109.8	109.1	178.9	89	*k*
CH_3CF_3	108.5	110.6	178.4	89	*l*
CH_3SiH_3	109.3	107.7	176.5	88	*m*
CH_3GeH_3	108.3	108.4	175.6	88	*n*
FCH_2CF_3	109	108.9	177.4	89	*o*
$ClCH_2CF_3$	109.5	108	177.2	89	*p*
average				89 ± 1	
		3-Coordinated			
CH_3^+	108.7	120	188.3	94	*q*
$H_2C{=}CH_2$	108.7	117.4	185.8	93	*r*
$CH_2{=}C{=}CH_2$	108.2	118.4	185.8	93	*s*
$H_2C{=}CF_2$	109.1	122.0	190.8	95	*t*
$H_2C{=}CMe_2$	109.5	117.4	187.1	94	*u*
$H_2C{=}C(Cl)CN$	108.6	116.5	184.7	92	*v*
$H_2C{=}CHF$	108.5	114.7	183.1	92	*w*
$H_2C{=}NH$	109.2	109.8	178.7	89	*x*
H_2CO	110.1	116.3	187	94	*y*
H_2CS	109.2	117.2	186.4	93	*z*
average				94 ± 1	

[a] Distances in pm and angles in degrees. [b] Ohno, K.; Matsuura, H.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *118*, 1. [c] Hirota, E.; Endo, Y.; Saito, S.; Duncan, J. L. *J. Mol. Spectrosc.* **1981**, *89*, 285. [d] Edgell, W. F.; Parts, L. *J. Am. Chem. Soc.* **1956**, *78*, 2358. [e] Lide, D. R. *J. Am. Chem. Soc.* **1952**, *74*, 3548. [f] Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864. [g] Davis, R. W.; Robiette, A. G.; Gerry, M. C. *J. Mol. Spectrosc.* **1981**, *85*, 399. [h] Muller, N. *J. Am. Chem. Soc.* **1953**, *75*, 860. [i] Chadwick, D.; Millen, D. J. *J. Mol. Struct.* **1975**, *25*, 216. [j] Iijima, T.; Jimbo, H.; Taguchi, M. *J. Mol. Struct.* **1986**, *144*, 381. [k] Swalen, J. D. *J. Chem. Phys.* **1955**, *23*, 1739. [l] Edgell, W. F.; Miller, G. B.; Amy, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 2391. [m] Kilb, R. W.; Pierce, L. *J. Chem. Phys.* **1957**, *27*, 108. [n] Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1210. [o] Ogata, T.; Miki, Y. *J. Mol. Struct.* **1986**, *140*, 49. [p] Ogata, T.; Koike, K.; Suzuki, H. *J. Mol. Struct.* **1986**, *144*, 1. [q] Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Kreiner, W. A.; Oka, T. *J. Chem. Phys.***1988**, *88*, 666. [r] Hirota, E.; Endo, Y.; Saito, S.; Yoshida, K.; Yamaguchi, I. *J. Mol. Spectrosc.* **1981**, *89*, 223. [s] Almenningen, A.; Bastiansen, O.; Traetteberg, M. *Acta. Chem. Scand.* **1959**, *13*, 1699. [t] Mijlhoff,F. C.; Renes, G.; Kohata, K.; Oyanagi, K.; Kuchitsu, K. *J. Mol. Struct.* **1977**, *39*, 241. [u] Hilderbrandt, R. L.; Wieser, J. D. *J. Mol. Struct.* **1973**, *15*, 27. [v] Avirah, T. K.; Malloy, T. B.; Cook, R. L. *J. Mol. Struct.* **1975**, *26*, 267. [w] Carlos, J. L., Jr.; Karl, R. R., Jr.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177. [x] Pearson, R.; Lowas, F. T. *J. Chem. Phys.* **1977**, *66*, 4149. [y] Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177. [z] Turner, P. H.; Halonen, L.; Mills, I. M. *J. Mol. Spectrosc.* **1981**, *89*, 402.

The geometric parameters of molecules in which a central carbon atom is 4-coordinated and in which there are two or more hydrogen ligands are given in Table 2. The ligand radius of hydrogen bonded to 4-coordinate carbon has been deduced in each case from the H···H distance and has an average value of 89 pm. The consistency of the values obtained from a variety of simple molecules suggests strongly that the ligands are essentially close-packed in these molecules as we have previously found for the ligands F, O, and Cl. Table 2 also gives data for 3-coordinated molecules of carbon in which there are two or three H ligands. The

Table 3. NH Bond Lengths, HNH Bond Angles, and H···H Distances in Some Nitrogen Molecules[a]

	N−H	∠H−N−H	H···H	*r*(H)	ref
NH_4^+ Cl^-	103.2	109.5	168.6	84	*c*
NH_4^+ Br^-	103.1	109.5	168.4	84	*d*
NH_3	101.6	107.3	163.7	82	*e*
ND_3	101.4	107.1	163.1	82	*e*
D_3NBF_3	100.7	107.6	162.5	81	*f*
NH_2^-	103.4	104	163	82	*g*
H_2NCH_3	103.1	106	164.7	82	*h*
H_2NNH_2	102.2	107	164.3	82	*i*
H_2NF	102.3	103.5	160.7	80	*j*
H_2NBH_2[b]	99.5	112.6	165.6	83	*k*
H_2NBF_2	100.3	106.9	161.1	81	*l*
H_2NCl	101.7	107	164	83	*m*
H_2NSH[b]	99.5	110.1	163.1	82	*n*
average				82	

[a] Distances in pm and angles in degrees. [b] Ab initio structures. [c] Ibers, J. A.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *28*, 926. [d] Gutowsky, H. S.; Pake, G. E.; Bersohn, R. E. *J. Chem. Phys.* **1954**, *22*, 643. [e] Helminger, P.; De Lucia, F. C.; Gordy, W. *J. Mol. Spectroc.* **1971**, *39*, 94. [f] Penner, G. H.; Ruscitti, B.; Reynolds, J.; Swainson, I. *Inorg. Chem.* **2002**, *41*, 7064. [g] Mason, S. F. *J. Phys. Chem.* **1957**, *61*, 384. [h] Iijima, T.; Jimbo, H.; Taguchi, M. *J. Mol. Struct.* **1986**, *144*, 381. [i] Morino, Y.; Iijima, T.; Murata, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 46. [j] Christen, D.; Minkwitz, R.; Nass, R. *J. Am. Chem. Soc.* **1987**, *109*, 7020. [k] Dewar, M. J. S.; McKee, M. L. *J. Mol. Struct.* **1980**, *68*, 105. [l] Lovas, F. J.; Johnson, D. R. *J. Chem. Phys.* **1973**, *59*, 2347. [m] Cazzoli, G.; Lister, D. G.; Favero, P. G. *J. Mol. Spectrosc.* **1972**, *42*, 286. [n] Austen, M. Personal communication.

values of *r*(H) vary from 92 to 95 pm with an average value of 94 pm for the apparent ligand radius of H in these molecules. We conclude that in these 3-coordinated molecules the ligands are not quite close-packed. The value of 92 pm for the ligand radius of hydrogen bonded to carbon given previously by Bartell[1,2] was obtained from data for both 3- and 4-coordinated molecules. Our value of 89 pm applies only to molecules with 4-coordinated carbon in which the ligands may be considered to be close-packed.

Table 3 gives data for AX_4^+ and AX_3E molecules of nitrogen where at least two of the ligands are H. The average value for the ligand radius of H in the NX_4^+ molecules is 84 pm in close agreement with the average value of 82 pm for the NX_3E molecules confirming that a lone pair behaves just like ligands in that it repels the ligands until they are close-packed. The overall average value for the ligand radius of hydrogen bonded to N is 82 pm.

The only data available for determining the radius of hydrogen bonded to oxygen is that for the H_2O molecule in which the bond length is 95.7 pm, the bond angle 104.5°, and the H···H distance 151.4 pm, giving a radius of H bonded to O of 76 pm. Although the structures of a dozen or so H_3O^+ salts have been determined, in all cases the hydroxonium ion is strongly hydrogen bonded to other molecules or anions, is considerably distorted from the C_{3v} symmetry expected for an isolated H_3O^+ ion, and has bond angles varying from considerably smaller than 109.5° to considerably greater than this angle.[9]

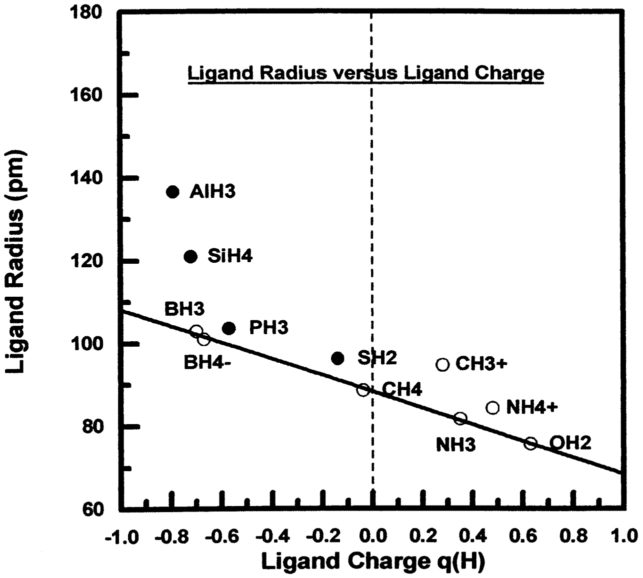

Figure 1. Plot of ligand radius versus ligand charge. The molecules in which the H ligands are close-packed fall on the straight line. Molecules in which the H ligands are not close-packed lie above this line.

Table 4. Ligand Radii (pm)

	central atom			
ligand	Be	B	C	N
H		102	89	82
C		137	125	120
N	144	124	119	
O	133	119	114	
F	126	113	108	107
Cl	168	151	145	140

Table 5. Ligand Radii and Atomic Charges for Hydrogen, Fluorine, and Chlorine in 4-Coordinated Molecules

	r(H)	*q*(H)[a]	*r*(F)	*q*(F)[a]	*r*(Cl)	*q*(Cl)[a]
BX_4^-	102	−0.67	113	−0.86	151	−0.7
CX_4	89	−0.04	108	−0.61	145	−0.09
NX_3E	82	0.35	106	−0.28	142	+0.24
OX_2E_2	76	0.63	110	−0.17	139	+0.33

[a] The atomic charges *q*(H), *q*(F), and *q*(Cl) were obtained by the AIM analysis of the electron density calculated by density functional theory at the B3LYP/G+(2d,p) level.

The average values of the ligand radius of hydrogen for the central atoms B, C, N, and O are summarized in Table 4 together with the previously determined radii for other ligands. In each case the ligand radius of hydrogen is smaller than that of any of these other ligands. In all cases the ligand radius decreases with increasing electronegativity of the central atom. This is because, as we have discussed previously,[4] the ligand radius is a function of the charge on the ligand which decreases from a negative value for boron to an almost zero value for carbon to an increasing positive value for nitrogen and oxygen, with increasing electronegativity of the central atom. Figure 1 gives a plot of the hydrogen ligand radius for BH_3, BH_4^-, CH_4, CH_3^+, NH_3, NH_4^+, and H_2O against the AIM atomic charge (Table 5). We see that the ligand radius decreases continuously as the ligand charge decreases from −0.67 for BH_3 and then becomes positive increasing to +0.63 for H_2O. The plot is linear through the points for BH_4^- (BH_3), CH_4, NH_3, and H_2O. The point for CH_3^+ lies well off the line, consistent with our conclusion that the H ligands in CH_3^+ are not truly

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Table 6. Comparison of Predicted and Calculated H···X Distances[a]

	A−H	A−X	∠H−X−H	∠H−A−X	∠X−A−X	H···H	X···X	H···X		ref
								obsd	pred[b]	
BH_3	118		120.0			205.2				*d*
BHF_2	118	131		120.9	118.2		224.0	216	215	*g*
BF_3		131			120.0		226.4			*h*
CH_4	109		109.5			177.2				*e*
CH_3F	111	139	109.9	109		180.9		203	197	*e*
CH_2F_2	109	136	111.9	108.1	108.3	181	220.1	200	197	*e*
CHF_3	109	135		110.5	108.5			200	197	*e*
CF_4		132			109.5		215.4			*i*
CH_3Cl	110	178	110.9	108		180.5		236	234	*e*
CH_2Cl_2	109	177	115.5	108.1	112.9	179.8	292.7	234	234	*e*
$CHCl_3$	107	177		108.5	110.4		290.2	234	234	*e*
CCl_4		177			109.5		289.3			*j*
CH_3Br	110	194	111.6	107.2		181.2		249	248	*e*
CH_2Br_2	107	192	110.9	108.3	112.9	176.4	321.7	248	248	*e*
$CHBr_3$	107	193		108.1	110.8		317.7	248	248	*e*
CBr_4[c]		194.2			109.5		317.2			*k*
NH_3	102		107.5			163.7				*f*
NH_2F	102	143	103.3	101.1		160.5		191	188	*f*
NHF_2	103	140		99.8		102.9		187	188	*l*
NF_3		136.5			102.4		214.7			*m*
NH_2Cl	101	175	107	103.7		164		222	224	*f*
NCl_3		175.9			107.1		283.0			*n*
H_2O	95.7		104.5			151.4				*o*
HOF	96.4	144		97.2				183	186	*p*
F_2O		141			103.3		221			*q*
HOCl	96.4	170		103.0				213	215	*r*
Cl_2O		169.6			110.9		278			*s*

[a] Distances in pm and angles in degrees. [b] From sum of ligand radii $r(H) + r(X)$ in Table 5. [c] $r(Br) = 159$ pm. [d] See Table 1. [e] See Table 2. [f] See Table 3. [g] Schneider, W. F.; Narula, C. K.; Nöth, H.; Burstein, B. E. *Inorg. Chem.* **1991**, *30*, 3919. [h] Yamamoto, S.; Kuwabara, R.; Takami, M.; Kuchitsu, K. *J. Mol. Spectrosc.* **1986**, *155*, 333. [i] Fink, M.; Schmiedekamp, C. W.; Gregory, D. *J. Chem. Phys.* **1976**, *71*, 5238. [j] Konaka, S.; Murata, Y.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1134. [k] Beagley, B.; Brown, D. P.; Freeman, J. M.; Tanaka, K. *J. Mol. Spectrosc.* **1974**, *20*. [l] Lide, D. R. *J. Chem. Phys.* **1963**, *38*, 456. [m] Sheridan, J.; Gordy, W. *Phys. Rev.* **1950**, *79*, 513. [n] Bürgi, H. B.; Stedman, D.; Bartell, L. S. *J. Mol. Struct.* **1971**, *10*, 31. [o] Laurie, V. W.; Herschbach, D. R. *J. Chem. Phys.* **1962**, *37*, 1687. Shibata, S.; Bartell, L. S. *J. Chem. Phys.* **1965**, *42*, 1147. [p] Kim, H.; Pearson, E. F.; Appelman, E. H. *J. Chem. Phys.* **1972**, *56*, 1. [q] Pierce, L.; Jackson, R. H.; DiCiani, N. *J. Chem. Phys.* **1961**, *35*, 2240. [r] Deeley, C. M. *J. Mol. Spectrosc.* **1987**, *122*, 481. [s] Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochman, F. *Advanced Inorganic Chemistry*; John Wiley: New York, 1999; p 560.

close-packed. This is not surprising in view of the much smaller radius of H bonded to carbon than of H bonded to boron. The point for NH_4^+ lies a little above the line, suggesting that again the H ligands are not quite close-packed, presumably because the lone pair in NH_3 exerts a slightly greater repulsive force than an H ligand, and consistent with our conclusion that a lone pair pushes the ligands togther until they "touch". It may be noted that the ligand radius of hydrogen decreases much more rapidly from boron to oxygen than does the radius of any other ligand. This is because the charge on H decreases much more rapidly than for other ligands as shown, for example, by the ligands fluorine and chlorine in Table 5.

It is interesting to note that the hydrogen ligand atomic charge varies continuously with the electronegativity of the ligand from Li to F and from Na to Cl (Figure 2) similarly to the fluorine ligand atomic charge that we studied previously.[4]

Further confirmation of the ligand radii of hydrogen can be obtained from a comparison of H···X nonbonding distances predicted from the sum of the ligand radii from Table 4 and the values calculated from experimental bond lengths and bond angles in molecules containing both H and X ligands. These are given in Table 6. The agreement between the predicted and observed values is very good in almost every case and provides further confirmation of the ligand radius of H for B, C, N, and O. For some fluorocarbon molecules the agreement between the observed H···F distances and those given by the sum of the ligand radii of H ands F is not quite so good, presumably because there is a significant variation of the charge on the F atom from molecule to molecule.

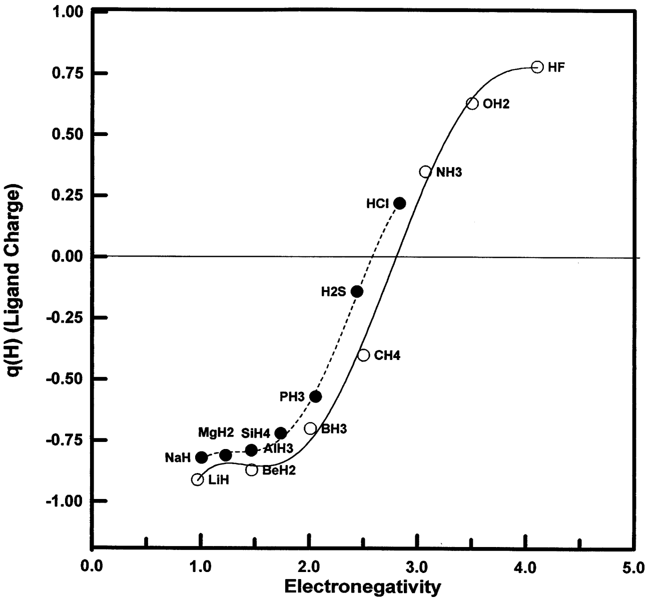

Figure 2. Plot of ligand charge against electronegativity (Allred−Rochow) for the period 2 and 3 hydrides.

Some of the examples in Table 6 show clearly the inadequacy of the VSEPR rule that states that bond angles decrease with increasing ligand electronegativity. For example, the bond angle in HOF (97.2°) is considerably smaller than in either H_2O (104.5°) or F_2O (103.3°) whereas the electronegativity rule would predict that it should be intermediate between these two angles. Similarly the bond angle in HOCl is smaller than in either H_2O or Cl_2O. However, these angles are consistent with ligand close-packing because as we have seen the predicted and observed H···X distances are in quite close agreement. An important reason for the superiority of the LCP model for predicting the bond angle is that it takes account of bond length differences while the VSEPR electronegativity rule does not. Using the F···H and Cl···H distances predicted from the sum of the ligand radii and the observed bond lengths we can predict the bond angle in HOF to be 100° and in HOCl to be 105°, in good agreement with the observed values 97° and 103°, respectively. We note also that the bond angle in Cl_2O (112.8°) is larger than in H_2O (104.5°) despite the greater electronegativity of Cl than H. For many molecules the electronegativity rule works well, as for example with the halogens where bond angles decrease in many molecules in the order $EABr_3 > EACl_3 > EAF_3$, because the size of the ligands decreases in the same order.

The angle in Cl_2O is not only larger than the angle in H_2O but also larger than the tetrahedral angle of 109.5° whereas, according to the VSEPR rule that lone pairs take up more space in the valence shell than bond pairs, the bond angle should be smaller than 109.5°. The large bond angle of 112.5° can be reasonably attributed to the size of the chlorine ligands. The VSEPR rule that lone pairs take up more space in the valence shell than bond pairs should be replaced by the rule that lone pairs repel ligands until they "touch", that is, until the interligand distance is equal to the sum of their ligand radii. Thus molecules with small ligands such as NH_3, NF_3, H_2O, and F_2O have bond angles smaller than the tetrahedral angle while larger ligands have bond angles that may be larger than the tetrahedral angle if the ligand is large enough, i.e., has a large enough ligand radius.

Period 3 Molecules. Attention has often been drawn to the very small bond angles in PH_3 (93.3°) and H_2S (92.1°) which are smaller than in the corresponding fluorides PF_3 (97.8°) and SF_2 (98.0°) and therefore in disagreement with the VSEPR electronegativity rule. As we will now see, these small angles are due to the small size of the H ligand. We have shown previously that the ligands in the molecules of the period 3 nonmetals are close-packed only in their six-coordinate molecules.[8] Because there are no known six-coordinate hydrides of the period 3 nonmetals, the ligand radius for hydrogen bonded to these atoms cannot be determined from experimental data. However, the radii can be estimated from the hydrogen atomic charges (Table 7) and the relationship between ligand radius and atomic charge (Figure 1). We see in Table 7 that the H···H interligand distance in SiH_4 calculated from the ligand charge is much smaller than the observed distance, confirming that the ligands are indeed not close-packed, as may also be seen in Figure 1 where the point for SiH_4 is well above the line through the ligand close-packed molecules. However, the calculated interligand distances for PH_3 and H_2S are much closer to the observed distance showing that the H ligands are nearly close-packed. Thus in these molecules the lone pair(s) push the ligands together until they are nearly close-packed, giving the observed small bond angles of 93.3° and 92.1°, respectively, which would be 88° and 87° for close-packing. This is also seen in Figure 1 where the points for PH_3 and H_2S lie just slightly above the line through the close-packed hydrides. The very small bond angles in PH_3 and H_2S are therefore not unexpected.

Table 7. Bond Lengths, Bond Angles, Interligand Distances, and Ligand Charges in Some Period 3 Hydrides

	A−H	∠H−A−H	q(H)	r(H)[a]	H···H		ref
					obsd	pred[b]	
SiH_4	147.3	109.5	−0.72	103	240	206	*c*
PH_3	141.1	93.3	−0.57	100	205.4	199	*d*
H_2S	133.6	92.1	−0.14	91	192.4	182	*e*

[a] From Figure 1 $r(H) = 88.3 - 19.9q$. [b] Predicted H···H = 2r(H). [c] Ohno, K.; Matsuura, H.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *118*, 1. [d] Kimura, K.; Tanaka, T. *J. Mol. Spectrosc.* **1986**, *118*, 1. [e] Edwards, T. H.; Moncur, N. K.; Snyder, L. E. *J. Chem. Phys.* **1967**, *46*, 2139.

Table 8. Bond Lengths, Bond Angles, and Interligand Distances in Hydrides of Groups 15 and 16[a]

	X−H	∠H−A−H	H···H	ref
PH_3	142.1	93.3	207	*b*
AsH_3	151.1	92.1	212	*c*
SbH_3	170	91.5	244	*d*
H_2S	133.6	92.1	192	*e*
H_2Se	146	90.6	208	*f*
H_2Te	165.8	90.2	235	*g*

[a] Distances in pm and angles in degrees. [b] Kimura, K.; Tanaka, T. *J. Mol. Spectrosc.* **1986**, *118*, 1. [c] Atwood, J. L.; Robinson, K. D.; Bennett, F. R.; Elms, F. M.; Koutsantonis, G. A.; Raston, C. L.; Young, D. J. *Inorg. Chem.* **1992**, *31*, 2673. [d] O'Hare, D.; Foord, J. S.; Page, T. C. M.; Whitaker, T. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1445. [e] Edwards, T. H.; Moncur, N. K.; Snyder, L. E. *J. Chem. Phys.* **1967**, *46*, 2139. [f] Hill, R. A.; Edwards, T. H. *J. Chem. Phys.* **1965**, *42*, 1391. [g] Moncur, N. K.; Willson, P. D.; Edwards, T. H. *J. Mol. Spectrosc.* **1974**, *52*, 380.

Although the H ligands in the hydrides of As, Sb, and Bi (Table 8) are not nearly close-packed, the bond angles in the hydrides decrease with increasing size of the central atom and the corresponding increase in bond length and the consequent reduction in the interligand repulsive forces. Each of these hydrides also has a smaller bond angle than the corresponding fluorides and chlorides (Table 9), consistent with the smaller size and correspondingly weaker interligand forces in the hydrides.

The VSEPR and LCP Models. Our results lead us to the conclusion that the effect of ligand electronegativity as postulated in the VSEPR model is a less useful explanation of bond angles than the LCP model, which explains bond angles in terms of the difference in the sizes of ligands as measured by their ligand radii and also takes into account differences in bond lengths. More generally, in molecules in which the ligands are not close-packed, bond angles are determined by the strength of the interligand repulsive forces, which may be considered to be roughly proportional to the ligand radii. From a qualitative point of view the two models

Table 9. Bond Lengths, Bond Angles, and Interligand Distances in Some Period 3 Fluorides and Chlorides[a]

	A−F	∠F−A−F	F···F	ref
PF_3	157.0	97.8	236.4	*b*
AsF_3	170.6	96.2	254.0	*c*
SbF_3	203	88	282	*d*
SF_2	159.2	98.2	241	*e*
SeF_2	169	94	247	*f*

	A−Cl	∠Cl−A−Cl	Cl···Cl	ref
PCl_3	204.0	100.4	313.2	*g*
$AsCl_3$	216.2	98.9	328.6	*h*
$SbCl_3$	233.3	97.2	350.0	*i*
SCl_2	200.6	103.0	314.3	*j*

[a] Distances in pm and angles in degrees. [b] Morino, Y.; Kuchitsu, K.; Motitani, T. *Inorg. Chem.* **1969**, *8*, 867. [c] Clippard, F. B., Jr.; Bartell, L. S. *Inorg. Chem.* **1970**, *9*, 905. [d] Bystrom, A.; Westgren, A. *Ark. Kemi, Mineral. Geol.* **1943**, *17B*, No 2. [e] Endo, Y.; Saito, S.; Hirota, E.; Chikaraishi, T. *J. Mol. Spectrosc.* **1979**, *77*, 222. [f] De Leew, D. M.; Mooyman, R.; De Lange, O. A. *Chem. Phys.* **1979**, *38*, 21. [g] Iwasaki, M.; Hedberg, K. *J. Chem. Phys.* **1962**, *36*, 589. [h] Konaka, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1693, 3107. [i] Konaka, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 404. [j] Morino, Y.; Murata, Y.; Ito, T.; Nakamura, J. *J. Phys. Soc. Jpn.* ***1962***, *17*, Suppl. BII, 37.

are essentially identical except that the VSEPR concept of bond-pair−bond-pair repulsion is replaced in the LCP model by ligand−ligand repulsion and the concept of ligand radius. Both models lead to the same conclusion that the angles between ligands are smaller than the angles between ligands and lone pairs. The VSEPR model considers that lone-pair−bond-pair repulsions are larger than bond-pair−bond-pair repulsions and justifies this on the grounds that a lone pair domain is larger than a bond pair domain because a lone pair domain spreads out as much as possible around the central core while a bonding domain is restricted to the region between the two bonded atoms (cores). The LCP model takes much the same view, namely, that a lone pair spreads out around the central core as much as possible, pushing the ligands together until they "touch", i.e., reach the $r(A) + r(B)$ distance.

The LCP model has the advantage that the distance between ligands can be predicted when the ligands are close-packed, for example when they are pushed together by a lone pair, whereas the decrease in the size of a bonding domain with increasing ligand electronegativity is a purely qualitative concept. It would be advantageous to modify the VSEPR model by replacing the assumed effect of ligand electronegativity on bond angles by the effect of ligand size on bond angles as described by the LCP model.

Calculations

Atomic charges were obtained by the AIM analysis[10,11] of electron densities calculated by density functional theory at the B3LYP/6-311+G(2d,p) level.

Summary and Conclusions

1. The hydrogen ligands may reasonably be considered to be close-packed in the four-coordinated molecules of B, C, N, and O as has been found previously for the ligands F, Cl, C, N, and O so that ligand radii may be estimated from ligand−ligand distances.

2. The hydrogen ligand radii are smaller than the ligand radii of F, Cl, C, N, and O when bonded to the same central atom so that H···H and H···X distances are smaller than X···X distances and the corresponding angles HAH and HAX angles are smaller than XAX angles. Because the A−H bond length is always smaller than the X−H bond length, HAX angles may also be smaller than either the HAH or XAX angles, as in the case of HOF.

3. The VSEPR assumption that angles XAY decrease with increasing electronegativity of the ligands X and Y is not correct for HAH and HAX angles when they are compared with other XAY angles. Nevertheless this assumption works well for many molecules because electronegativity generally decreases with increasing ligand size, as for example in the series F, Cl, Br.

4. The very small angles in PH_3 and H_2S are consistent with the small ligand radius of hydrogen and are a consequence of the lone pairs repelling the ligands until they are nearly close-packed.

5. While the VSEPR model remains a useful model, particularly for teaching in introductory courses because it is directly based on the simple Lewis model, the LCP model gives a more consistent and semiquantitative explanation of bond angles in molecules with lone pairs and/or more than one kind of ligand when the ligands are close-packed and provides an explanation for the small angles observed when hydrogen is a ligand.

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