$1.76P_1^{1/2}P_2^{-1/4}\lambda$ or $\rho_0 = 1.5P_2^{-1/2}\gamma$; this relation depends only upon the adequacy of the three relationships involved to describe the facts. In terms of our interpretation of equation 1, however, we must expect ρ_0 to be greater than γ, so that $P_2^{1/2}$ must be less than 1.5. This is consistent with the derivation of the equation, in which $P_2 \lesssim 1$ is the probability of reaction of H and HI upon encounter. For P_2 to be appreciably less than unity would make ρ_0 correspondingly greater than γ, which seems unlikely. The evidence suggests that $P_2 \sim 1$ from −25 to −196°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA]

Bond Angles and the Spatial Correlation of Electrons[1]

BY R. J. GILLESPIE

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Bond angles in various series of related molecules such as the hydrides and halides of Groups V and VI are discussed in terms of the spatial correlation of electron pairs that results from the operation of the Pauli exclusion principle. It is shown that a number of apparent anomalies can be understood in terms of the strong repulsions between electron pairs in the completely filled valency shells of first-row elements in contrast to the weaker repulsions associated with incompletely filled valency shells of other elements.

It has long been a problem to explain why the bond angles in the water and ammonia molecules are so close to the tetrahedral angle of 109.5° while the bond angles in phosphine, hydrogen sulfide and the other hydrides of these groups approach closely to 90°. Other related observations that have not been explained satisfactorily include the facts that, in contrast to the corresponding hydrides, the bond angle in NF_3 is smaller than in PF_3, that the fluorides of elements such as P and As have anomalously large bond angles when compared with the other halides of these elements and that the valency angle at an oxygen atom is, in a variety of molecules, considerably larger than at the sulfur atom in the corresponding molecule. It is the purpose of this paper to show that some understanding of these bond angle variations can be obtained by considering the spatial correlation of electron pairs in valency shells which arises mainly from the operation of the Pauli Exclusion Principle.

The Hydrides of Groups V and VI.—The valence-bond theory in its simplest form assumes that the bonds in molecules such as NH_3 and H_2O are formed by p orbitals on the central atom and it predicts therefore that the bond angles in these molecules should be 90°.[2] The bond angles in PH_3 and H_2S and the higher members of both groups of molecules are in reasonably good agreement with this predicted value, being generally just a few degrees larger than 90°, but the bond angles in the water and ammonia molecules are very much larger and approach the tetrahedral angle (Table I).[3,4] Repulsions between the hydrogen atoms and partial hybridization of the orbitals of the central atom have been put forward as explanations of these apparently anomalous bond angles in NH_3 and H_2O, but neither is completely satisfactory.[2,5,6] It is not altogether clear why these same factors are not also important in the higher members of each group: indeed, hybridization might be expected to become an increasingly important factor as the energy difference between s and p orbitals becomes smaller with increasing atomic number of the central atom.

TABLE I

HYDRIDES OF GROUPS V AND VI

Molecule	Bond angle	Ref.	Molecule	Bond angle	Ref.
H_3N	107.3	3	H_2O	104.5	3
H_3P	93.3	3	H_2S	92.2	3
H_3As	91.8	3	H_2Se	91.0	4a
H_3Sb	91.3	3	H_2Te	89.5	4b

An alternative explanation of the shapes of these molecules has been put forward recently based on the idea that the arrangement of all the electron pairs (bonding pairs *and* lone pairs) in the valency shell of the central atom is determined by the operation of the Pauli exclusion principle,[7,8] as a consequence of which the electrons in a valency shell arrange themselves in close pairs of opposite spin which keep as far apart as possible. For four electron pairs this leads to a tetrahedral arrangement,[7] and this is the most probable arrangement of the four pairs of electrons in the outer or valency shells of the ions C^{4-}, N^{3-} and O^{2-}. These electron pairs may to a reasonable approximation be regarded as each independently occupying one of four tetrahedrally directed equivalent segments of a sphere surrounding the nucleus and inner electron shells, which may be conveniently described as tetrahedral orbitals and are essentially the sp^3 hybrid orbitals introduced in the valence-bond theory.[2] Figure 1 shows the most

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[1] Presented at the 138th meeting of the American Chemical Society in New York, September 1960.

[2] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 108–124.

[3] L. E. Sutton, "Interatomic Distances," Chemical Society Special Publication No. 11, 1958.

[4] (a) A. W. Jache, P. W. Moser and W. Gordy, *J. Chem. Phys.*, **25**, 209 (1956); (b) K. Rossman and J. W. Straley, *ibid.*, **24**, 1276 (1956).

[5] C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 171.

[6] R. S. Mulliken, THIS JOURNAL, **77**, 887 (1955).

[7] (a) J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1037 (1951); (b) C. E. Mellish and J. W. Linnett, *ibid.*, **50**, 657 (1954); (c) P. G. Dickens and J. W. Linnett, *ibid.*, **53**, 1037 (1957); (d) P. G. Dickens and J. W. Linnett, *Quart. Rev. Chem. Soc.*, **11**, 291 (1957); (e) J. L. Lennard-Jones, *J. Chem. Phys.*, **22**, 1087 (1952); (f) A. Brickstock and J. A. Pople, *Phil. Mag.*, **44**, 705 (1953).

[8] R. J. Gillespie and R. S. Nyholm, *Quart. Rev. Chem. Soc.*, **11**, 339 (1957).

probable arrangement of three electron pairs in a plane and the corresponding trigonal orbitals which are essentially the same as the sp^2 hybrid orbitals of valence-bond theory. The explicit form given by the valence-bond theory to the shapes of such orbitals is only an approximation and is not necessarily much more exact than the shapes indicated in Fig. 1. In any case the exact form of these orbitals is not important for our discussion.

When an electron pair is used to form a bond with a hydrogen nucleus, the motions of the electrons are somewhat restricted by the electrostatic attraction of the proton and the electrons will tend to be more concentrated along the direction of the internuclear axis. Thus an electron in a lone-pair orbital may be described as occupying a rather large and diffuse "pear-shaped" orbital while a bonding electron pair may be described as occupying a somewhat more restricted and smaller "sausage-shaped" orbital. As the electrons in a lone-pair orbital can therefore come closer to electrons in another orbital than can electrons in a smaller more restricted bonding orbital, it follows that lone-pair electrons will, as a consequence of both Pauli and electrostatic forces, exert greater repulsions on other electron pairs than will bonding electrons.[7b,8] In CH_4 and NH_4^+ all the electron pairs occupy equivalent bonding orbitals and exert exactly equal repulsions on each other; hence these molecules have a regular tetrahedral shape. On passing from CH_4 to NH_3 and replacing a bonding electron-pair by a lone pair, the repulsions between the electron pairs are no longer exactly the same and the somewhat greater repulsion exerted by the lone-pair electrons pushes the bonding pairs slightly closer together thereby decreasing the bond angle. On passing from NH_3 to H_2O another bonding pair is replaced by a lone pair and the bond angle again decreases correspondingly.[7b] The analagous situation for the trigonal planar arrangement of three electron pairs one of which is a lone pair is shown in Fig. 1.

Because the electronegativity of P is less than that of N and its radius is greater, the bonding electrons in PH_3 will be further from the central nucleus and closer to the hydrogen nuclei than in NH_3. Thus the bonding electron pairs are at a greater distance apart and occupy more restricted "sausage-shaped" orbitals in PH_3 than in NH_3. Repulsions between the bonding pairs are therefore smaller, and between the lone pair and the bonding pairs relatively greater, than in NH_3. Hence the bond angle in PH_3 is smaller than in NH_3. A similar and probably smaller effect is expected on passing to the higher members of the series.[7b] Similar considerations also apply to H_2O, H_2S, etc. However these arguments do not entirely satisfactorily account for why there is such a large decrease in the bond angle from NH_3 to PH_3 and only a very small further decrease on passing to the higher members of each series and why the bond angles for the later members of the series are so close to 90°.

A reasonable explanation of this large decrease in bond angle between the first and second members of each of these groups of molecules can be obtained if it is remembered that the valency shell of the "light" elements (*i.e.*, the elements of the first short period Li–Ne) is complete when it contains four pairs of electrons while the valency shells of the "heavy" elements (*i.e.*, the elements of the second and subsequent rows of the periodic table) can accommodate more than four electron pairs. The maximum coordination number of the "light" elements is four and the valency shell of these elements is completely filled by four electron pairs, or, in other words, the orbitals occupied by these electrons essentially occupy all the space around the atom. Pauli forces are of such a nature that if the electron pairs occupy separate orbitals that do not overlap appreciably the repulsion between them is very small, but if the orbitals are brought close together so that they begin to overlap appreciably, then the force between them rapidly becomes very large, *i.e.*, Pauli forces can be represented as varying approximately as some large inverse power of the inter-electron distance.[9] Thus in the filled valency shell of first-row elements there would be expected to be considerable resistance to distortions of the bond angles as this would cause overlap of the electron orbitals and consequent strong repulsions. Experimentally it is found that the deviations from the tetrahedral angle in the molecules of "light" elements with completed valency shell is rarely more than a few degrees. In the second and subsequent rows of the periodic table, however, the maximum coördination number is greater than four, *i.e.*, the valency shell can accommodate more than four electron pairs. The M quantum shell can contain up to a maximum of nine electron pairs but this maximum is never reached when the M shell is an outer or valency shell, and under these circumstances it is, in fact, never found to contain more than six electron pairs (either bonding or nonbonding). It seems reasonable to suppose therefore that as a consequence of the Pauli exclusion principle a maximum of six electron pairs can be accommodated in the M shell when it is an outer or valency shell and that these six electron pairs effectively occupy all the space in the M shell. The most probable arrangement of six equivalent electron pairs is at the corners of a regular octahedron[8,10,11]; they may be regarded as occupying six octahedrally directed segments of a sphere

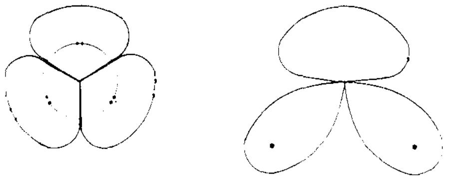

Fig. 1.—(A) Most probable spatial distribution and corresponding trigonal orbitals for three electron pairs confined to a plane; . ., most probable positions of electron pairs. (B) Orbitals for two bonding electron pairs and one lone-pair; ●, nuclei of bonded atoms.

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[9] K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, N. Y., 1953, p. 319.

[10] J. W. Linnett and C. E. Mellish, *Trans. Faraday Soc.*, **50**, 665 (1954).

[11] R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

surrounding the nucleus and inner electron shells, *i.e.*, six octahedral orbitals directed at right angles to each other which are essentially the sp^3d^2 orbitals of valence-bond theory. Thus for the "light" elements repulsions between any two electron pairs become large when they make an angle of approximately 109.5° at the nucleus and more than four electron pairs cannot be accommodated in their valency shells as this would considerably reduce this angle. On the other hand for elements of the second short period, presumably because of the greater volume available in the valency shell, repulsions between electron pairs do not become of importance until they make an angle of 90° with the nucleus and a maximum of six electron pairs can be accommodated in the valency shells of these elements. Thus in passing from, say, SiH_4 to PH_3 the greater repulsions exerted by the lone pair in PH_3 causes a considerable distortion of the bond angle as the bonding pairs do not begin to repell each other appreciably until the angle they make with the nucleus approaches 90°. The repulsions exerted by the two lone-pairs in H_2S should similarly cause the bond angle to approach 90°, and it would be expected to be slightly smaller than the angle of PH_3. However, when the valency shell contains the maximum number of six electron pairs, only relatively small distortions of the bond angles are possible as in the case of first-row elements with four electron pairs in their valency shell. Thus in BrF_5 and SbF_5^{-2} the single lone pair causes the bond angles[3,12] to be just a few degrees less than 90° which may be compared with the approximately 15° distortion that occurs when the valency shell contains only four electron pairs as in PH_3.

In the first long period the same restriction to a maximum of six electron pairs in the valency shell appears to hold and coördination numbers greater than six are not observed for elements such as As, Se and Br. Thus we expect that the bond angles in the molecules H_2Se and H_3As will be approximately 90°. Because of the smaller electronegativity of the central atom, the greater size of the valency shell and correspondingly greater ease of distortion of the tetrahedral arrangement of the four electron pairs, it would be expected that the angles would be slightly smaller than in H_2S and PH_3.

Some of the elements of the second long period can achieve coördination numbers up to eight and this may be regarded as the maximum number of electron pairs that can be accommodated in the valency shell of these elements. The most probable arrangement of eight such electron pairs is at the corners of a square antiprism,[11] and the angles between the electron pairs are then 75°. However these high coördination numbers are only achieved with very electronegative elements such as fluorine and oxygen which considerably shrink the size of the orbitals occupied by the bonding electrons, and it is not unreasonable to think that in combination with a less electronegative element such as hydrogen, and when some of the electrons are lone-pairs, repulsions between the bonding electron-pairs may still become of reasonable magnitude at an angle of approximately 90°. It is interesting to note that the bond angle in H_2Te has recently been reported[4b] to be slightly less than 90°.

Halides of Groups V and VI.—Substitution of hydrogen by fluorine decreases the bond angle[3] from 104.5° in H_2O to 103.2° in F_2O and from 107.3° in NH_3 to 102.1° in NF_3 in agreement with the supposition that the more electronegative fluorine contracts the orbitals occupied by the bonding electrons more than hydrogen and these orbitals therefore repell each other less and move closer together as a consequence of the relatively greater repulsions exerted by the lone-pairs.

In the series of molecules PF_3, PCl_3, PBr_3, PI_3 and AsF_3, $AsCl_3$, $AsBr_3$, AsI_3, because of the decreasing electronegativity and increasing size of the halogen atom, it might be predicted that the bond angle would increase steadily from the fluoride to the iodide and that the angle for the fluoride would be less than that for the corresponding hydride as discussed above. It may be seen from Tables I and II that the fluorides are anomalous and have much larger bond angles than expected. A similar anomaly is found in the series NF_3, PF_3, AsF_3, where the bond angle has a maximum value at PF_3 instead of decreasing continuously from NF_3 to AsF_3. In general it is found that apparently anomalous bond angles occur whenever a "light" element (in this case fluorine), with a completed valency shell of four electron pairs, is bonded to "heavy" element with an incomplete valency shell of four electron pairs. It seems very probable that the strong repulsions between the electron pairs on the fluorine atoms causes them to be partially delocalized into the partly empty shell of the "heavy" atom, or in other words, there is partial double bonding between the fluorine and the "heavy" atom. Because of the increased electron density in such a partial double bond it will repell other bonds more strongly than single bonds repell each other and bond angles involving such bonds will be larger than would be predicted for the corresponding single bonds.[8] The same tendency to double bonding will not be shown to the same extent by the other halogens as their valency shells are not complete with only four electron pairs. The repulsions between the electron pairs in such incomplete shells will be small and there will therefore not be the same tendency for them to delocalize into the similarly partly empty shell of the central atom. In other words it is suggested that the large electron pair repulsions in fluorine compared with the other halogens causes

TABLE II

BOND ANGLES[3] FOR GROUP V HALIDES

NF_3	PF_3	AsF_3	
102.1	104	102	
	PCl_3	$AsCl_3$	$SbCl_3$
	100.0	98.4	99.5
	PBr_3	$AsBr_3$	$SbBr_3$
	101.5	100.5	97
	PI_3	AsI_3	SbI_3
	102	101	99

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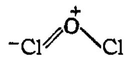
(12) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **27**, 982 (1957).

the contribution of structures such as (I) to be considerably more important in the fluorides than in the other halides

I

The well-known order for the mesomeric effect of the halogens in organic compounds,[13] F > Cl > Br > I, has essentially the same cause. The strong repulsions between the electron pairs in the completed valency shell of the fluorine atom causes at least one of these electron pairs to delocalize into a conjugated double bond or aromatic system more readily than an electron pair in the incomplete valency shells of the other halogens.

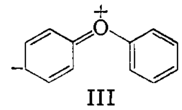
Bond Angles at O, S, Se and Te.—Oxygen should show the same tendency to delocalize its electron pairs as fluorine and it should therefore give large bond angles when it is attached to a "heavy" atom with an incomplete valency shell. The bond angle[3] in OCl_2 is 110.8° and is greater than in both F_2O (103.2°) and H_2O (104.5°), although it might have been expected to have been smaller than the latter. Although this large bond angle in Cl_2O could be attributed to repulsions between non-bonding electrons on different chlorine atoms, it is also consistent with the supposition that the strong repulsions between the electron pairs on the oxygen causes delocalization of these electrons into the partly vacant shell of the chlorine atom giving the bonds some partial double-bond character and hence increasing the interbond repulsions and the bond angle. This delocalization of the oxygen lone pairs may be described as a contribution from structures such as (II)



II

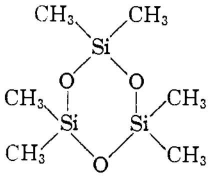
If oxygen is replaced by sulfur however, to give SCl_2, the bond angle decreases to 102° as there is no longer any great tendency for the electron pairs of the central atom to delocalize.

When oxygen is attached to saturated carbon or nitrogen, the bond angle at oxygen is within a few degrees of the tetrahedral angle in every case (except for small ring compounds which involve "bent" bonds) and is generally slightly smaller than the tetrahedral angle due to lone-pair repulsions being greater than bond-pair repulsions. When oxygen is attached to an aromatic ring however, as in diphenyl ether, the lone-pair electrons on the oxygen can partially delocalize into the aromatic system, the O–C bonds acquire some double-bond character (III) and the bond angle increases to values considerably greater than the tetrahedral angle (Table III). For S, Se and Te, however, there is no great tendency for their lone-pair electrons to delocalize into an aromatic system, and therefore the bond angles in diarylsulphides and related compounds are smaller than the tetrahedral angle.

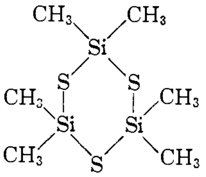


III

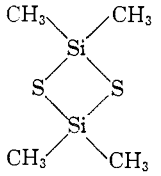
When oxygen and nitrogen are attached to "heavy" atoms with incomplete valency shells, delocalization of the lone-pair electrons on the oxygen or nitrogen into the valency shell of the "heavy" atom occurs, just as it does into an aromatic system, with a similar increase in bond angle. Thus the SiOSi angle generally falls in the range 130–140° and the $N(SiH_3)_3$ molecule is planar with 120° bond angle. It has been suggested by several authors[14] that these large bond angles are due to pπ-dπ bonding between N or O and silicon. Other examples of XOX bond angles where X is a "heavy" atom are collected in Table III. It may be seen that they are consistently larger than the tetrahedral angle. When oxygen is replaced by S, Se or Te, it is found that the XSX, XSeX and XTeX bond angles (where X is a "heavy" element) are consistently smaller than the tetrahedral angle and often approach 90° as in H_2S. Some examples are given in Table III. The possibility of a smaller valency angle at S leads, in several cases, to the structure of a sulfur compound differing from the oxygen analog. Thus although both the trimeric hexamethylcyclotrisiloxane (IV) and hexamethylcyclotrisilthiane (V) are known (note that the SiOSi angle is greater than the SiSSi angle), of the corresponding dimeric compounds only the sulphur compound, tetramethylcyclodisilthian (VI) is known. The structure of this molecule necessitates a valency angle at S of 90° or less. The observed value is 75°. The bonds here may be slightly bent and the angle between the bonding electron pairs may in fact be somewhat greater than 75°. It is evident that oxygen, with its complete valency shell and with its tendency to delocalize its lone pair electrons into the Si valency shell, could not achieve such a small bond angle. It is also interesting that the five-membered ring compound (VII) is reported[24] to be considerably more strained than cyclopentane, and this would be consistent with the SiOSi angle being larger than the tetrahedral angle.



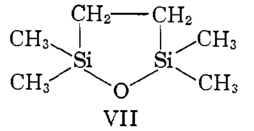
IV



V



VI



VII

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(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 77.

(14) (a) K. Hedburg, THIS JOURNAL, **77**, 6491 (1955); (b) D. P. Craig, A. MacColl, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); (c) R. C. Lord, D. W. Robinson and W. C. Schumb, THIS JOURNAL, **78**, 1327 (1956).

(15) D. E. C. Corbridge, *Acta Cryst.*, **9**, 308 (1956).

(16) D. MacArthur and C. A. Beevers, *ibid.*, **10**, 428 (1957).

TABLE III

COMPARISON OF XOX, XSX, XSeX AND XTeX BOND ANGLES[3,15-23]

C_{Al}–O–C_{Al}		C_{Al}–S–C_{Al}		C_{Al}–Se–C_{Al}			
$(C_2H_5)_2O$	108	$(CF_3)_2S$	105.6	$(CF_3)_2Se$	104.4		
$(CH_3)_2O$	110	$(CH_3)_2S$	105	$(CH_3)_2Se$	98		
1:4 Dioxan	108	1:4 Dithian	100	1:4 Diselenan	97.6		
Paraldehyde	109.5	Tristhioacetaldehyde	106.5				
		Methionine	100				
C_{Ar}–O–C_{Ar}		C_{Ar}–S–C_{Ar}		C_{Ar}–Se–C_{Ar}		C_{Ar}–Te–C_{Ar}	
p-$C_6H_4(OCH_3)_2$	121	(p-$CH_3C_6H_4)_2S$	109	(p-$CH_3C_6H_4)_2Se$	106	(p-$CH_3C_6H_4)_2Te$	101
(p-$IC_6H_4)_2O$	123	(p-$BrC_6H_4)_2S$	109				
(p-$BrC_6H_4)_2O$	123						
$(C_6H_5)_2O$	124						
Si–O–Si		Si–S–S					
α-Quartz	142	$(SiS_2)_n$	90				
$(SiO_3^{2-})_n$	137.5						
$(Cl_3Si)_2O$	130						
$(CH_3Si)_2O$	140						
$(CH_3)_2Si_2O$	137	$(CH_3)_4Si_2S_2$	75				
$[(CH_3)_3Si]_2O$	125	$[(CH_3)_2SiS]_3$	110				
P–O–P		P–S–P		P–Se–P			
P_4O_6	129						
P_4O_{10}	124	P_4S_{10}	109.5				
$(P_4O_{12})^{4-}$	132	P_4S_3	102	P_4Se_3	100[19]		
$(PO_3)_n^{n-}$	129[15]	P_4S_5	107[21]				
$P_2O_7^{4-}$	134[16]	P_4S_7	106				
$P_3O_{10}^{5-}$	121[17]	$P_4S_3I_2$	104[18]				
As–O–As		As–S–As					
As_4O_6	126	As_4S_6	100				
		As_4S_4	100				
Sb–O–Sb		Sb–S–Sb		Sb–Se–Sb			
Sb_4O_6	130	SbSBr	96[20]	Sb_2Se_3	95[22]		
S–O–S		S–S–S		S–Se–S		S–Te–S	
$(SO_3)_3$	114	S_8	105				
$(SO_3)_n$	121	S_n	100				
$HS_2O_7^-$	114	S_4^{2-}	104.5				
$S_3O_{10}^{-2}$	122	$(C_6H_5SO_2)_2S$	106.5	$(C_6H_5SO_2)_2Se$	105	$(C_6H_5SO_2)_2Te$	97
		$(CH_3SO_2S)_2$	104			$(Cu_3SO_3S)_2Te$	100
		$S_4O_6^{--}$	103			$(Cu_3C_6H_4SO_2S)_2Te$	96
		$S_5O_6^{--}$	106	$SeS_4O_6^{--}$	101	$TeS_4O_6^{--}$	103
Se–O–Se		Se–Se–Se					
SeO_2	125	Se_8	105.3				
Cr–O–Cr							
$(CrO_3)_n$	136						
$(Cr_2O_7)^{-2}$	115						
Ru–O–Ru							
$(Cl_5Ru)_2O$	180						
Ti–O–Ti							
$[TiCl_2(C_5H_5)]_2O$	180[23]						

The POP bond angle in P_4O_6 is 129°, in P_4O_{10} 124° and in the tetrametaphosphate ion $P_4O_{12}^{-4}$ 132°. In each case it is considerably greater than the tetrahedral angle due to partial double-bond character of the P–O–P bonds resulting from delocalization of the oxygen lone-pair electrons. On the other hand in P_4S_{10} the PSP angle is 109° and P_4S_6 does not exist, although there are other sulfides, *e.g.*, P_4S_3, P_4S_5 and P_4S_7, which have no oxygen analogs, in which the PSP angles are 102°, 107° and 106° respectively. Thus the tendency for the oxygen valency angle to be greater than tetrahedral when bonded to P and for the S valency angle to be less than tetrahedral when bonded to P can be regarded as at least partly responsible for the nonexistence of P_4S_6 where the valency angle tends to be approximately tetrahedral and the existence, on the other hand, of the molecules P_4S_3, P_4S_5 and P_4S_7, which have no oxygen analogs, where the sulphur valency angle is smaller than tetrahedral. Similarly in As_4O_6 the AsOAs angle is 126° while in As_4S_6 it is only 100° and arsenic also forms the sulphide As_4S_4, which has oxygen analog, and in which the AsSAs angle is only 100°.

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(17) (a) D. R. Davies and D. E. C. Corbridge, *ibid.*, **11**, 315 (1958); (b) D. E. C. Corbridge, *ibid.*, **12**, 263 (1960).

(18) D. A. Wright and B. R. Penfold, *ibid.*, **12**, 455 (1959).

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Conclusions.—(1) For "light" elements containing four electron pairs in their valency shells the angles between bonds formed to hydrogen or to other "light" elements will be approximately tetrahedral and will generally differ only by a few degrees from this value.

(2) For "heavy" elements containing only four electron pairs in their valency shells the angles between bonds formed to hydrogen or to other "heavy" elements will be smaller than tetrahedral and will often approach 90°.

(3) For "light" elements forming bonds to "heavy" elements with vacant orbitals in their valency shells the angles between these bonds will in general be larger and often considerably larger than the tetrahedral angle.

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Proton Magnetic Resonance Spectra of Some Ethyl Compounds

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The proton magnetic resonance spectra of zinc diethyl, germanium tetraethyl, dichlorodiethylsilane and trichloroethylsilane have been studied at both 40 and 60 Mcs. Except for $SiCl_2(C_2H_5)_2$, the values of the internal chemical shift δ and the spin–spin coupling constant J between the methyl and methylene group protons in these compounds have been obtained from a complete analysis of the spectra as A_3B_2 systems. A simple method of obtaining the value of δ from complex A_3B_2 type spectra is outlined. The δ values in the series $Si(C_2H_5)_4$–$SiCl_3(C_2H_5)$ appear to vary linearly with the number of chlorine atoms attached to silicon. The problem of correlating δ values with electronegativity, x, of the substituents is discussed in the light of presently available data on several ethyl compounds of the type $X(C_2H_5)_n$.

Introduction

The proton magnetic resonance spectra of several ethyl compounds have been studied,[2–14] and attempts have been made to correlate the internal chemical shift δ between the methyl and methylene protons in the ethyl group with the electro-negativity, x, of the group or atom attached to this ethyl group.[2,3,7–9,11,14–16] An empirical linear relationship between δ and x was suggested by Dailey and Shoolery[3] which fit the data for the ethyl halides, but it was later noted by Shoolery[15] that for substituents of lower electronegativity one of the empirical constants of the equation had to be adjusted.

A linear correlation of electronegativity x with chemical shift δ might be expected if the inductive effect of the substituent were the predominant mechanism for altering the charge about the methylene protons and if the methyl group were relatively unaffected. However, chemical shielding effects arising from the magnetic anisotropy of the C–X bond, or from mesomerism, would cause deviations from this simple relationship.[4,9]

In the present investigation we have obtained δ values for two ethyl compounds with substituents of low electronegativity, $Zn(C_2H_5)_2$ and $Ge(C_2H_5)_4$, as well as for the pair $SiCl_2(C_2H_5)_2$ and $SiCl_3(C_2H_5)$ in which the effect of increasing chlorine substitution could be noted. A revised interpretation of the spectrum observed[14] for $Ga(C_2H_5)_3$ is included since the method developed for this purpose provides a precise general technique for extracting δ from the complex A_3B_2 (ethyl) spectra arising when the ratio J/δ is not small. Finally, we have used all available data from $X(C_2H_5)_n$ spectra to discuss the problem of correlating δ with electronegativity.

Experimental

The proton magnetic resonance spectra of $Zn(C_2H_5)_2$, $Ge(C_2H_5)_4$, $SiCl_2(C_2H_5)_2$ and $SiCl_3(C_2H_5)$ were obtained using liquid samples in sealed tubes (5 mm. o.d.). The samples were degassed before sealing and the spectra were recorded with a Varian V-4300 spectrometer (40 Mcs.) and at 60 Mcs. with a V-4311 r.f. unit. The usual spinning and sideband modulation techniques were employed.

Results

The experimental spectra along with the theoretically calculated spectra are given in Figs. 1–4 for the compounds studied. Although the spectra were obtained at both 40 and 60 mcs. for all the compounds studied, we have given here the experimental and theoretical spectra for only one of these two frequencies for each compound. The theoretical spectra were calculated in the manner outlined elsewhere.[11] The results are summarized in Table I. The proton magnetic resonance spectrum of $SiCl_2(C_2H_5)_2$ at 40 mcs. is a single line (slightly broadened) while at 60 mcs. some structure is seen. The δ value given in Table I for this compound is obtained from an approximate fit of the theoretical spectrum to the experimental spectrum at 60 mcs. assuming the value J = 8.0 c.p.s., a value found for

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