(Polymers Program, Division of Materials Research). Thanks are also due the Dow Corning Corp., for the PDMS samples and for the sabbatical leave granted to J.R.F.

References and Notes

(1) (a) University of Michigan. (b) University of Michigan. (c) University of Cincinnati.
(2) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(3) L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd ed., Clarendon Press, Oxford, 1975.
(4) B. E. Eichinger, *Macromolecules*, **5**, 496 (1972).
(5) W. W. Graessley, *Macromolecules*, **8**, 186, 865 (1975).
(6) G. Ronca and G. Allegra, *J. Chem. Phys.*, **63**, 4990 (1975).
(7) K. J. Smith, Jr., and R. J. Gaylord, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2069 (1975).
(8) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **351** 351 (1976).
(9) R. T. Deam and S. F. Edwards, *Philos. Trans. R. Soc. London, Ser. A*, **280**, 317 (1976).
(10) P. J. Flory, *J. Chem. Phys.*, **66**, 5720 (1977).
(11) P. J. Flory, *Macromolecules*, **12**, 119 (1979).
(12) D. J. Walsh, G. Allend, and G. Ballard, *Polymer*, **15**, 366 (1974); G. Allen, P. A. Holmes, and D. J. Walsh, *Faraday Discuss. Chem. Soc.*, **57**, 19 (1974); G. Allen, P. L. Egerton, and D. J. Walsh, *Polymer*, **17**, 65 (1976); J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *J. Chem. Phys.*, **70**, 5324 (1979).
(13) J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
(14) E. M. Valles and C. W. Macosko in "Chemistry and Properties of Crosslinked Polymers", S. S. Labana, Ed., Academic Press, New York, 1977.
(15) J. E. Herz, P. Rempp, and W. Borchard, *Adv. Polym. Sci.*, **26**, 105 (1978), and pertinent references cited therein.
(16) L. M. Dossin and W. W. Graessley, *Macromolecules*, **12**, 123 (1979).
(17) J. E. Mark, R. R. Rahalkar, and J. L. Sullivan, *J. Chem. Phys.*, **70**, 1794 (1979).
(18) J. E. Mark, *Macromol. Rev.*, **11**, 135 (1976).
(19) R. C. Smith, N. C. Angelotti, and C. L. Hanson in "Analysis of Silicones", A. L. Smith, Ed., Wiley-Interscience, New York, 1974.
(20) W. T. Grubb and R. C. Osthoff, *J. Am. Chem. Soc.*, **77**, 1405 (1955).
(21) J. C. Saam and F. W. G. Fearon, U.S. Patent 3 678 125 (1972).
(22) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Wiley-Interscience, New York, 1962.
(23) M. L. Dunham, D. L. Bailey, and R. Y. Mixer, *Ind. Eng. Chem.*, **49**, 1373 (1957).
(24) P. G. Bork and C. W. Roush in "Vulcanization of Elastomers", G. Alliger and I. J. Sjothun, Eds., Reinhold, New York, 1964.
(25) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).
(26) J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970).
(27) T.-K. Su and J. E. Mark, *Macromolecules*, **10**, 120 (1977).
(28) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
(29) J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
(30) P. F. Flory and Y. Tatara, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 683 (1975).
(31) M. Mooney, *J. Appl. Phys.*, **19**, 434 (1948); R. S. Rivlin, *Philos. Trans. R. Soc. London, Ser. A*, **241**, 379 (1948).
(32) Very similar results were obtained when the segregated groups were placed at approximately every sixth unit at the ends of the chains (J. R. Falender, manuscript in preparation). This indicates that the vinyl-$Si[OSi(CH_3)_2H]_4$ cross-linking reaction is not very significantly affected by vinyl-vinyl proximity effects.
(33) C. U. Yu and J. E. Mark, *Polym. J.*, **7**, 101 (1975).
(34) M. A. Llorente and J. E. Mark, *J. Chem. Phys.*, **71**, 682 (1979).
(35) The preliminary results published previously [*Polym. Prepr.*, **19**, 743 (1978)] were calculated using swelling equation parameters now thought to be less appropriate than those used in the present analysis.

Dependence of Bond Angles upon the Steric Effect. 1. XMX Bond Angles

Marvin Charton

Contribution from the Chemistry Department, Pratt Institute,
Brooklyn, New York 11205.

Received June 4, 1979

Abstract: Bond angles X-M-X in tetrahedral and trigonal planar species are generally dependent on steric effects. This is shown by the success of correlations with the equation $1/\sin(\theta_X/2) = b_0(1/r_{VX}) + b_1$, where $\theta_X = \angle XMX$ and r_{VX} is the van der Waals radius of X, and $1/\sin(\theta_X/2) = d_1 r_{VM} + d_0$, where r_{VM} is the van der Waals radius of M. The correlation equations are useful for the prediction of bond angles. H atoms bonded to O, N, or C do not fit the steric effect model. Groups X capable of $d\pi$–$p\pi$ bonding also do not fit the model.

The valence shell electron pair repulsion (VSEPR) theory has been very widely used in the prediction of the shape of a chemical species on the basis of repulsions between electron pairs.[1] The theory does not successfully account for the deviation of the observed bond angles in many compounds from the predicted geometry. These deviations, although small, are experimentally significant. According to VSEPR theory, they are due to the electronegativity of the substituents attached to the central atom. Searcy has attempted to predict bond angles from an electrostatic model.[2]

An alternative viewpoint has been presented[3] which suggests that in many cases the observed bond angles can be accounted for by interactions between nonbonded atoms. This proposal has been criticized by Wilson[4] on the grounds that equally good predictions in the case of trigonal planar carbon compounds could be made by simply assuming average values for the bond angles. Nonbonded interactions have been used recently to account for the geometry of a number of species. In this work we present evidence based on a very simple model which suggests that generally bond angles are determined by steric effects (nonbonded atom repulsions).

Consider the structural fragment X^1–M–X^2 shown in Figure 1, where $X^1 = X^2$, X is some atom or group of atoms, and M is a central atom to which the two X groups are bonded. If the bond angle is determined by the size of the X group, the two X groups will be in contact, and the distance $\overline{XA}$ from the X nucleus to the point A at which the X groups are in contact will be equal to the van der Waals radius of X if X is monatomic. If X is polyatomic, the distance $\overline{XA}$ will be from the group center to the point in contact and will be given by the group van der Waals radius, r_{VX}. The distance $\overline{XM}$ is simply the XM bond length. As triangles X^1AM and X^2AM are congruent, angle X^2MA is equal to angle X^1MA and designating angle X^1MX^2 as θ

$$X^1MA = \theta_X/2 \tag{1}$$

Then

$$r_{VX} = l_{MX} \sin(\theta_X/2) \tag{2}$$

$$1/\sin(\theta_X/2) = l_{MX}/r_{VX} \tag{3}$$

We may write

$$l_{MX} = r_{CM} + r_{CX} \tag{4}$$

where r_{CM} and r_{CX} are the covalent radii of M and X, respectively. We have shown elsewhere[5] that as suggested by

0002-7863/79/1501-7356$01.00/0

Table I. Results of Correlations with Equations 8, 9, and 15

set	b_0 or C_1	b_1 or G	r^a	F^b	$s_{est}{}^c$	$s_{b_0}{}^c$	$s_{b_1}{}^c$	$100r^2$ [d]	n^e
01[f]	1.00	−0.349	0.9814	157.1	0.0488	0.0798	0.131	96.32	8
1	0.590	0.872	0.9680	89.40	0.0139	0.0624	0.0326	93.71	8
2	0.268	1.169	0.9727	87.86	0.0118	0.0286	0.0153	94.62	7
3	0.230	1.211	0.9318	19.78[g]	0.0154	0.0518[h]	0.0307	86.83	5
13	0.377	1.011	0.9159	20.83[g]	0.0289	0.0826[i]	0.0455	83.89	6
14	0.267	1.151	0.9781	110.3	0.006 98	0.0254	0.0158	95.66	7
15	0.255	1.176	0.9909	217.0	0.005 18	0.0173	0.0106	98.19	6
16	0.254	1.186	0.9978	916.6	0.002 51	0.008 38	0.005 14	99.57	6
21	0.328	1.114	0.9644	39.92[j]	0.0151	0.0519[j]	0.0326	93.01	5
22	0.285	1.184	0.9164	10.49[m]	0.009 24	0.0881[m]	0.0524[j]	83.98	4
31	0.336	1.069	0.8509	5.249[k]	0.0154	0.147[l]	0.0872[j]	72.41	4
32	0.410	1.033	0.7947	6.855[m]	0.0178	0.157[m]	0.0935	63.15	6
33	0.423	0.949	0.9184	10.78[m]	0.0188	0.129[m]	0.0749[j]	84.35	4
34	0.317	1.022	0.9633	90.15	0.006 20	0.0334	0.0189	92.79	9
35	0.444	0.933	0.9572	21.86[h]	0.0138	0.0949[h]	0.0552[j]	91.62	4
36	0.149	1.128	0.9401	30.43[j]	0.004 32	0.0269[j]	0.0151	88.38	6
151	0.150	1.113	0.9540	30.41[g]	0.005 86	0.0272[n]	0.0512	91.02	5
152	0.376	0.636	0.9970	496.4	0.005 69	0.0169	0.0290	99.40	5
153	0.207	0.960	0.9958	357.5	0.003 87	0.0110	0.1090	99.17	5
154	0.291	0.781	0.9910	164.6	0.008 02	0.0227[j]	0.0393	98.21	5
155	0.440	0.486	0.9744	56.34	0.0225	0.0586[j]	0.103[n]	94.94	5
156	0.320	0.716	0.9972	177.6[h]	0.001 70	0.0240[h]	0.0444[h]	99.44	3
157	0.270	0.802	0.9890	44.55[m]	0.002 86	0.0404[m]	0.0748[m]	97.80	3
161	0.229	0.819	0.9972	534.8	0.004 58	0.009 92	0.0176	99.44	5

[a] Correlation coefficient. [b] F test for significance of correlation. The superscript indicates the confidence level (CL). No superscript indicates a CL of 99.9%. [c] Standard errors of the estimate, b_0, and b_1. The superscript indicates CL of the Student's t test for the significance of the coefficient. No superscript signifies CL of 99.9%. [d] The percent of the variance of the data accounted for by the correlation equation. [e] The number of points in the set. [f] For set 01, b_0 is C_1, b_1 is C_0. [g] 97.5% CL. [h] 95.0% CL. [i] 98.0% CL. [j] 99.0% CL. [k] <90.0% CL. [l] 80.0% CL. [m] 90.0% CL. [n] 98.0% CL.

Table II. Values of r_V and r_A

X	r_V	$r_A{}^q$	X	r_V	$r_A{}^q$	X	r_V	M	r_V
H	1.20[a]	0.85	SiH_3	1.90[e]	1.55	SCN	2.09[h]	O	1.52[a]
F	1.47[a]	1.12	$SiMe_3$	2.60[e]	2.25	NMe_2	1.63[i]	S	1.80[a]
Cl	1.75[a]	1.40	GeH_3	1.92[e]	1.57	PF_2	1.84[j]	Se	1.90[a]
Br	1.85[a]	1.50	OCF_3	2.19[f]	1.84	OPh	1.77[k]	Te	2.06[a]
I	1.98[a]	1.63	SCF_3	2.62[f]	2.27	1-aziridinyl	1.59[l]	N	1.55[a]
Me	1.72[b]	1.37	$SCCl_3$	2.91[f]	2.56	NH_2	1.55[m]	P	1.80[a]
Et	1.76[c]	1.41	ClO_3	2.18[e]	1.83	OMe	1.56[n]	As	1.85[a]
CF_3	2.11[b]	1.76	CN	1.60[a]	1.25	OEt	1.68[n]	Sb	1.90[o]
SO_3^-	2.19[b]	1.84	C_2H	1.78[a]	1.43	$OCH{=}CH_2$	1.76[k]	Bi	1.87[p]
SO_2F	2.19[d]	1.84	SMe	1.84[g]		PO_3^{2-}	2.24[e]		

[a] Bondi, A. *J. Phys. Chem.* **1964,** *68*, 441. [b] Charton, M. *J. Am. Chem. Soc.* **1969,** *91*, 615. $r_{V,min} \perp$ values. [c] From $\upsilon_X = r_{VX} - 1.20$ (see eq 18) and υ_{Et} reported in Charton, M. *J. Am. Chem. Soc.* **1975,** *97*, 1552. [d] Assumed equal to r_{V,SO_3^-} as the two groups are essentially isosteric. [e] Calculated $r_{V,min} \perp$ values as described in footnote *b*. [f] Calculated from the extended branching equation and eq 18; Charton, M. Abstracts, 1st Conference on Correlation Analysis in Organic Chemistry, Assisi, 1979. [g] From eq 18 and υ_{SMe} reported in Charton, M.; Charton, B. 1. *J. Org. Chem.* **1978,** *43*, 1161. [h] From the υ value of CH_2CN and eq 18. SCN and CH_2CN are assumed to be isosteric. [i] From eq 18 and υ_{NMe_2} reported in Charton, M. *J. Org. Chem.* **1977,** *42*, 3535. [j] The value must lie between r_{V,PH_2} and r_{V,PMe_2}. We have shown elsewhere that for $X = MH_n(lp)_{3-n}$ where $n = 1$ or 2, $r_{VX} = r_{VM}$ (eq 19). $r_{V,MNe_2} - r_{V,NH_2} = 0.08$. Assuming that the effect of the substitution on P is analogous to that on N, $r_{V,PMe_2} = 1.88$. From eq 19, $r_{V,PH_2} = 1.80$. Then, r_{V,PF_2} must lie between 1.80 and 1.88. We have chosen 1.84 as a reasonable value. [k] From υ_{OX} calculated from the equation $\upsilon_{OX} = 0.959\ \upsilon_{CH_2X} - 0.100$: Charton, M. *J. Org. Chem.* **1977,** *42*, 3531. [l] $\upsilon_{1\text{-aziridinyl}}$ must lie between υ_{NH_2} and υ_{NMe_2}, for which the values are 0.35 and 0.43, respectively. A reasonable value is 0.39, which gives, from eq 18, an r_V value of 1.59. [m] From eq 19. [n] From the reference in footnote *k*. [o] Calculated from the correlation equation for set 151 and the HSbH angle in SbH_3 (see footnote *b*, Table III). [p] Calculated from the correlation equation for set 152 and the MeBiMe bond angle in Me_3Bi. Beagley, B.; McAloon, K. T. J. *J. Mol. Struct.* **1973,** *17*, 429. [q] Calculated from the correlation equation for set 01, Table 1.

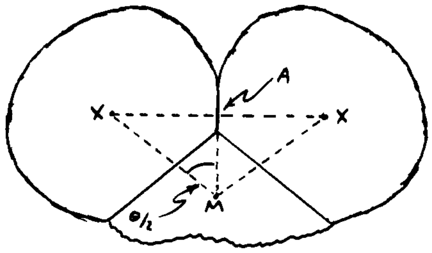

Figure 1.

Pauling:[6]

$$r_{VX} = a_1 r_{CZ} + a_0 \tag{5}$$

or

$$r_{CZ} = (1/a_1)r_{VZ} - (a_0/a_1) \tag{5a}$$

Then

$$l_{MX} = b_1 r_{VX} + r_{CM} - (a_0/a_1) \tag{6}$$

$$= b_1 r_{VX} + b_0 \tag{7}$$

where

$$b_1 = 1/a_1 \tag{7a}$$

Table III. Bond Angles and Deviations Obtained with Equation 8

			1A				
set	$MX_2{}^1X$	Me[a,c]	ClO_3[a,d]	H	Et	F[a,e]	
1	$O(lp)_2$ $\angle_{obsd}$	111.72(0.33)	118.6(0.7)	104.52	108(3)	103.3	
	$\angle_{calcd}$	110.8	122.1	94.3	111.9	103.5	
	Δ[b]	0.9	3.5	10.2	3.9	0.2	
	CF_3[a,f]	Cl[a]	SO_2F[a,g]	OCF_3[a,f]	SO_3^-[a,h]	PF_2[i]	
	124.0(0.6)	110.8(1)	123.6(0.5)	120.(1)	124.2	135.2	
	120.5	111.6	122.3	122.3	122.3	114.0	
	3.5	0.8	1.3	2.3	1.9	21.2	
2	$S(lp)_2$	H[a]	Cl	CF_3	CF_3S[a]	Me[a,j]	
		92.25	103.0	105.6(3)	103.8(3)	98.9(0.2)	
		91.8	98.3	101.0	103.7	98.0	
		0.4	4.7	4.6	0.1	0.9	
	MeS	CN[k]	GeH_3[a,l]	NMe_2[m]	Me_3Si[a,n]	SiH_3[a,o]	Cl_3CS[a,p]
	104(5)	96, 98.37, 102.1	98.9(0.3)	116(1)	104	97.4(0.72)	106(0.5)
	99.1	96.9	99.7	97.2	103.6	99.5	104.9
	4.9	0.9, 1.5, 5.2	0.8	18.8	0.4	2.1	1.1
3	$Se(lp)_2$	GeH_3[u]	H[a]	SCN[a]	CN[r]	CF_3[a,s]	
		94.6(0.5)	91(0.6)	101	99	97.0[a](2)	
		97.4	91.1	98.4	95.1	98.5	
		2.8	0.1	2.6	3.9	1.5, 4.4	
		SiH_3[a,t]	Me[a,q]				
		96.6(0.7)	96.2(0.2)				
		97.3	96.1(0.1)				
		0.7					
34	CH_2	H	CN[a,v]	F[a,w]		1[a]	
		109.5	110.4(0.4)	108.3(0.05)		114.7	
		102.1	110.1	107.8		115.6	
		7.4	0.3	0.5		0.9	
	Et[a]	Cl[a,w]	Br[a,w]	Me[a,x]		SiH_3[a,y]	SO_3^-[a,z]
	112.9(0.2)	111.8(0.2)	112.7(0.5)	112.4(0.2)		114.4	119.7
	112.6	112.5	113.9	112.0		114.5	118.0
	0.3	0.7	1.2	0.4		0.1	1.7
				1B			
set	$MX_1{}^1X_2$	X	Me[a,aa]	H[a,aa]	CF_3[a,aa]	F[a,aa]	1[a]
21	$P(lp),PX_2$	∠obsd	99.6	91.3	103.8	99.1	102.3
		∠calcd	100.1	92.3	103.9	96.8	102.8
			0.5	1.0	0.1	2.3	0.5
22	S(lp)O	Cl[a,bb]	F[a]	Br[a]	Me[a,cc]	NMe_2[m]	
		96.1(0.7)	92.8(1)	96(2)	96.57	96.9(1.2)	
		96.0	93.2	96.8	95.72	94.8	
		0.1	0.4	0.8	0.8	2.1	
				1C			
set	MX^1	CF_3[a]	Me[a,dd]	Et[a]	H	F[a]	
13	N(lp)	114(3)	110.6(0.6)	113(3)	106.69	102.5(1.5)	
		112.8	107.4	108.0	98.0	102.9	
		1.2	3.2	5.0	6.7	0.4	
	Cl[a,ee]	CF_3S[a,ff]	SiH_3				
	107.1(0.3)	118.8(0.2)	119.6(0.7)				
	107.8	118.1	110.1				
	0.7	0.7	0.5				
14	P(lp)	OMe[qq]	1[a,gg]	H[a]		Cl[a,gg]	
		119.2(1.1)	102	93.3(0.2)		100.3	
		98.3	102.1	93.5		100.2	
		20.9	0.1	0.2		0.1	
	Br[a,gg]	GeH_3[pp]	OEt[oo]	SiH_3[nn]		Me[a,hh]	
	101.5	95.39(0.005)	120.0(1.0)	96.45(0.5)		98.6(0.3)	
	101.1	101.6	99.5	101.5		99.9	
	0.4	6.2	20.5	6.5		1.3	
	CF_3[hh]	NMe_2[ii]	$OCH{=}CH_2$	CN[jj]		C_2H[a,kk]	
	97.2(0.3)	96	124.0(1.0)	93.5(2)		101(2)	
	103.0	99.0	100.3	98.7		100.5	
	5.8	3	23.7	5.2		0.5	
15	As(lp)	Br[a,ll]	Cl[a]	F[a,ll]		H[a]	
		99.66(0.26)	98.4(0.5)	96.1(0.2)		91.83(0.33)	
		99.14	98.3	95.6		92.15	
		0.5	0.1	0.5		0.3	
	1[a,ll]	CF_3[a]	Me	SiH_3[mm]		CN[ss]	
	100.2(0.1)	100.1(3.5)	96(5)	93.78(0.17)		91.5(3.5), 87(9.5)	
	100.1	100.9	98.1	99.51		97.0	
	0.1	0.8	2.1	5.7		5.5, 9.4	

Table III (*Continued*)

16	Sb(lp)	Cl[a,ll]	Br[a,gg]	F[a,gg]	H[a]	I[a,ll]	CF_3[a]
		97.0	98.2	95.0	91.30(0.33)	99.1(2)	100.0(3.5)
		97.4	98.2	94.8	91.4	99.1	99.9
		0.4	0	0.2	0.1	0	0.1
31	P, O	MeO	F[a,tt]	Cl[a,tt]	Br[a]	Me[a,uu]	PhO[rr]
		118.4(1.6)	101.3(0.2)	103.3(0.2)	108(3)	104.1(0.6)	104,96.6
		102.3	100.8	105.0	106.2	104.6	105.2
		16.1	0.5	1.7	1.8	0.5	1.2; 8.6
32	P, S	F[a]	Cl[a,tt]	Br[a]	Me[a,uu]	Et[a]	1-aziridine[a,vv]
		100.3(2)	101.8(0.2)	106(3)	104.4(0.2)	107	100(1.7)
		99.3	104.2	105.7	103.7	104.4	101.5
		1.0	2.4	0.3	0.7	2.6	1.5
36	C, H	F[a]	Cl[a,ww]	Me[a,xx]	H	Br[a]	CF_3[yy]
		108.8(0.75)	111.3(0.2)	111.15(0.1)	109.5	110.8(0.3)	112.9(0.2)
		108.8	111.1	110.89	105.8	111.8	113.1
		0.1	0.3	0.3	3.5	0.9	0.2

			2		
set	M, X¹				
33	C, O	F[a,aaa]	Cl[a]	H[bbb]		Br
		108.0(0.5)	111.3(0.1)	115.83(0.33)		110(5)
		107.9	114.3	100.4		116.3
		0.1	3.0	15.4		6.3
		Me[a,zz]	CF_3[a,zz]	NH_2		
		116.7(0.3)	121.4(0.4)	117.0(0.3)		
		113.65	120.9	109.9		
		3.1	0.5	7.1		
35	C, CH_2	CF_3[a,zz]	F[a,aaa]	H	Me[a,ccc]	Cl[a]
		123.6(0.3)	109.1(0.4)	117.57(0.5)	112	114.5(1)
		122.0	108.1	100.27	114.2	114.9
		1.6	1.0	17.30	2.2	0.4

[a] Included in correlation. [b] Unless otherwise noted, angle is from Sutton, L. E., Ed. "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958; "Supplement 1956–1959". [c] Blukis, W.; Kasai, P. H.; Myers, R. *J. Chem. Phys.* **1963,** *38,* 2753. [b] Beagley, B. *Trans. Faraday Soc.* **1965,** *61,* 1821. [e] Pierce, L.; DiCianni, N. *J. Chem. Phys.* **1963,** *38,* 730. Pierce, L.; Jackson, R. H.; DiCianni, N. *Ibid.* **1961,** *35,* 2240. Bauer, S. H. Abstracts, 3rd Austin Symposium on Gas Phase Molecular Structure, March 1970; personal communication. [g] Hencher, J. L.; Bauer, S. H. *Can. J. Chem.* **1973,** *51,* 2047. [h] Lynton, H.; Truter, M. R. *J. Chem. Soc.* **1960,** 5112. [i] Yow, H. Y.; Rudolph, R. W. *J. Mol. Struct.* **1975,** *28,* 205. [j] Hayashi, M.; Pierce, L. *Spectrochim. Acta, Part A* **1960,** *16,* 1272. [k] Linke, K. H.; Lemmer, F. *Z. Anorg. Allg. Chem.* **1966,** *345,* 203. Arnold, W.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsch.* **1964,** *19,* 1428. Pierce, L.; Nelson, R.; Thomas, C. *J. Chem. Phys.* **1965,** *43,* 3423. [l] Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Cradock, S. *J. Chem. Soc. A* **1970,** 315. [m] Hargittai, I.; Hargittai, M. *Acta Crystallogr., Sect. A* **1969,** *25,* 5165. [n] Kriegsmann, H. *Ber. Bunsenges. Phys. Chem.* **1957,** *61,* 1088. [o] Almenningen, A.; Hedberg, K.; Seip, R. *Acta Chem. Scand.* **1963,** *17,* 2264. [p] Berthold, H. J. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1961,** *116,* 290. [q] Beecher, J. F. *J. Mol. Spectrosc.* **1966,** *21,* 414. [r] Linke, K. H.; Lemmer, F. *Z. Anorg. Allg. Chem.* **1966,** *345,* 211. [s] Marsden, C. J.; Sheldrick, G. M. *J. Mol. Struct.* **1971,** *10,* 405. [t] Almenningen, A.; Fernhold, L.; Seip, H. M. *Acta Chem. Scand.* **1968,** *22,* 51. [u] Murdock, J. D.; Rankin, D. W. H.; Glidewell, C. *J. Mol. Struct.* **1971,** *9,* 17. [v] Hirota, E.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1960,** *33,* 158, 705. [w] Chadwick, D.; Millen, D. J. *Trans. Faraday Soc.* **1971,** *67,* 1539. [x] Lide, D. R., Jr. *J. Chem. Phys.* **1960,** *33,* 1514. [y] Almenningen, A.; Seip, R.; Seip, H. M. *Acta Chem. Scand.* **1970,** *24,* 1697. [z] Truter, M. R. *J. Chem. Soc.* **1962,** 3393. [aa] Carley, A. J.; Cragg, R. H.; Smith, J. D. *Annu. Rep. Prog. Chem., Sect. A* **1975,** *72,* 129. [bb] Hargittai, I. *Acta Chem. Scand.* **1969,** *60,* 231. [cc] Feder, W.; Dreizler, H.; Rudolph, H. D.; Typke, V. *Z. Naturforsch. A* **1962,** *24,* 266. [dd] Beagley, B.; Hewitt, T. G. *Trans. Faraday Soc.* **1968,** *64,* 2561. [ee] Burgi, H. B.; Stedman, D.; Bartell, L. S. *J. Mol. Struct.* **1971,** *10,* 31. [ff] Marsden, C. I.; Bartell, L. S. *J. Chem. Soc., Dalton Trans.* **1977,** 1581. [gg] Kuchitsu, K. *MTP Int. Rev. Sci.: Phys. Chem., Ser. One 2,* 203. [hh] Marsden, C. J.; Bartell, L. S. *Inorg. Chem.* **1976,** *15,* 2713. [ii] Vilkov, L. V.; Khaikin, L. S. *Zh. Strukt. Khim.* **1969,** *10,* 978. [jj] Emerson, K.; Britton, D. *Acta Crystallogr.* **1964,** *17,* 1134. [kk] Kroon, J.; Mulscher, J. B.; Peerdeman, A. F. *J. Mol. Struct.* **1971,** *7,* 217. [ll] Morino, Y.; Kuchitsu, K.; Moritani, T. *Inorg. Chem.* **1969,** *8,* 867. [mm] Beagley, B.; Robiette, A. G. E.; Sheldrick, G. M. *J. Chem. Soc. A* **1968,** 3006. [nn] Beagley, B.; Robiette, A. G.; Sheldrick. G. M. *Ibid.* **1968,** 3002. [oo] Khaikin, L. S.; Vilkov, L. V. *Zh. Struct. Khim.* **1969,** *10,* 722. [pp] Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Hewitt, T. G. *J. Inorg. Nucl. Chem.* **1969,** *31,* 2351. [qq] Oberhammer, H., private communication cited by reference in footnote *i.* [rr] Svetich, G. W.; Caughlan, N. C. *Acta Crystallogr.* **1965,** *19,* 645. [ss] Emerson, K.; Britton, D. *Ibid.* **1963,** *16,* 113. [tt] Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971,** *10,* 344. [uu] Wilkins, C. J.; Hagen, K.; Hedberg, L.; Shen, Q.; Hedberg, K. *J. Am. Chem. Soc.* **1975,** *97,* 6352. [vv] Subramanion, E.; Trotter, J. *J. Chem. Soc. A* **1969,** 2309. [ww] Jen, M.; Lide, D. R. *J. Chem. Phys.* **1962,** *36,* 2525. [xx] Lide, D. R. *Ibid.* **1960,** *33,* 1519. [yy] Andreassen, A. L.; Bauer, S. H. *Ibid.* **1972,** *56,* 3802. [zz] Hilderbrandt, R. L.; Andreassen, A. L.; Bauer, S. H. *J. Phys. Chem.* **1970,** *74,* 1586. [aaa] Laurie, V. W.; Pence, D. T.; Jackson, R. H. *J. Chem. Phys.* **1962,** *37,* 2995. [bbb] Oka, T. *J. Phys. Soc. Jpn.* **1960,** *15,* 2274. [ccc] Bartell, L. S.; Bonham, R. A. *J. Chem. Phys.* **1960,** *32,* 824. [ddd] Laurie, V. W.; Pence, D. T. *Ibid.* **1963,** *38,* 2693.

and from eq 3

$$1/\sin(\theta_X/2) = (b_0/r_{VX}) + b_1 \qquad (8)$$

It has been argued by Bartell[3a] and more recently by Glidewell[3c] that the radii used to estimate bond angles should be half the distance between X groups in suitable model compounds. These radii are termed one-angle radii, r_A, and $r_{CX} < r_{AX} < r_{VX}$. We have correlated the r_A values reported by Glidewell with the r_V values of Bondi[7] by means of the equation

$$r_{AX} = C_1 r_{VX} + C_0 \qquad (9)$$

with excellent results. The statistics are reported in Table I (Set 01). They show that r_{AX} is linear in r_{VX} with $C_1 = 1.000$ and $C_0 = -0.349$. If the proposal of Bartell and Glidewell is correct, then $\overline{XA}$ is equal to r_{AX} and

$$1/\sin(\theta/2) = l_{MX}/r_{AX} \qquad (10)$$

From eq 7 and 9, with $C_1 = 1.00$

$$\frac{1}{\sin(\theta_X/2)} = \frac{(b_0/B_1C_0)}{r_{VX} + C_0} + b_1 \tag{11}$$

$$= \frac{b_2}{r_{AX}} + b_1 \tag{12}$$

We have examined the correlation[8] of sets of $1/\sin(\theta_X/2)$ values obtained from the XMX bond angles reported in the literature with $1/r_V$ and with (in some cases) $1/r_A$ values. The r_V values for single atoms were taken from the work of Bondi,[7] or, in the case of polyatomic groups, were $r_{V,\min}$ values calculated as described in previous work.[9] The r_A values are from Glidewell[3c] or were calculated from eq 9. As equally good correlations were generally obtained with either r_V or r_A, we have chosen to use the r_V values. The steric parameters used are set forth in Table II. The results of the correlations with eq 8 are given in Table I; those obtained with eq 12 are given in Table I of the supplementary material. The sets studied may conveniently be divided into two classes.

1. The species has tetrahedral geometry according to VSEPR theory. As we are considering only species which include the XMX structural unit, there are three possible subclasses: (A) $MX_2X^1_2$ where X^1 is constant and may be a lone pair (lp) or a substituent in all three subclasses; (B) $MX_2X^1X^2$ where X^2 is a constant substituent; (C) MX_3X^1.

2. The species has trigonal planar geometry according to VSEPR theory. Compounds of this type have the structure MX_2X^1 where X^1 is a constant substituent. The data used in the correlations are reported in Table III.

We have examined three sets of type 1A in which X^1 is a lone pair with M = O, S, and Se (sets 1, 2, 3) and one set with X^1 = H, M = C (set 34). Excellent correlation was obtained for set 1 when X = H was excluded. We have also generally excluded from all the correlations bond angles with errors equal to or larger than 3°. The bond angles observed are compared with the calculated bond angles for a number of groups in Table III; with the exception of the values for X = H and PF_2, all of the calculated values are within 4° of the observed values. Overall, the agreement is excellent. The large deviation of the PF_2 and H groups will be discussed below. Set 2 also gave an excellent correlation. The value for CN was not included in the correlation as no grounds were available for choosing among the values given in the literature. Good agreement with two of the literature values was obtained. The values for Cl, CF_3, and MeS show a large deviation. Of these, the experimental error reported for the MeS and CF_3 groups is very large and probably accounts for the discrepancy. The deviation of the Cl value is inexplicable at present. A very large deviation is obtained for the dimethylamino group. This will be discussed below.

Good correlation was obtained for set 3 with deviations less than 3° for all groups except CN. It must be noted that another value of the bond angle has been reported for CF_3; the deviation from this value is large. Excellent results were obtained for set 34 with deviations less than 2° except for X = H.

Two sets of type 1B were studied, with M = P, X^1 = lp, X^2 = PX_2 (set 21) and with M = S, X^1 = lp, X^2 = 0 (sets 21 and 22). Significant correlations with eq 8 resulted. The observed angles are generally in excellent agreement with the calculated angles shown in Table III.

Seven sets of type 1C have been examined. In five of these, the "constant substituent" is a lone pair (sets 13-16). M is N, P, As, and Sb, respectively. Significant correlations were obtained with eq 8 for all four sets. Comparison of calculated and observed bond angles for set 13 shows good agreement for all X other than Me, Et, H, and SiH_3. The deviation of the Et angle is not unexpected in view of the large reported error. The deviation of the Me value is surprising. In the case in which X = H or SiH_3, the size of the deviation clearly shows that this angle does not fit a steric model. Some other factor or factors must be involved. For set 14, very good agreement is obtained for all groups except CN, CF_3, and SiH_3, which do not fit the model, and NMe_2, which shows very large deviations. In set 15, only CN and SiH_3 deviated greatly. All of the members of set 16 gave excellent agreement between calculated and observed angles.

Of the three other sets of type 1C (sets 36, 31, and 32; the constant substituent is H, O, and S, respectively) two gave significant correlation with eq 8. The failure of set 31 to give significant results is probably due to the lack of a sufficient number of points in the set and the small range of $1/r_{VX}$ covered by the available points. For set 36, where X^1 = H and M = C, the only deviation is for X = H; otherwise agreement between calculated and observed values is excellent. For set 32, where X^1 = S and M = P, calculated and observed values are in good agreement for all points. Even in set 31, which did not give a significant correlation, the agreement between calculated and observed values is very good, with the exception of one of the angles reported for X = OPh in an X-ray study in which two widely divergent angles were found.

Finally, two sets of type 2 were studied (sets 33 and 35 with X^1 = O and CH_2, respectively). Both sets give significant correlations with eq 8. In set 33, major deviations were observed for X = NH_2, Br, and H. In the case of the NH_2 group, the angle was determined in an X-ray diffraction study and the large deviation may be due to intermolecular hydrogen bonding in the crystal. The large deviation observed when X = Br is reasonable in view of the large experimental error reported in the determination of the angle. The deviation obtained when X = H shows that in this case the steric effect model is obviously inapplicable and again some other factor or factors must be involved. All of the members of set 35 give very good agreement between calculated and observed bond angles except the H atom. Here once again, the model fails completely.

We may now consider the variation of ∠XMX as a function of M. From eq 4 and 5a with X constant

$$l_{MX} = b_1 r_{VM} + b_0' \tag{13}$$

where b_0' is $r_{CX} - (a_0/a_1)$. Then from eq 3 and 13

$$1/\sin(\theta_X/2) = \frac{b_1 r_{VM} + b_0'}{r_{VX}} \tag{14}$$

and

$$1/\sin(\theta_X/2) = d_1 r_{VM} + d_0 \tag{15}$$

We have examined the correlation of bond angles for sets (with constant X) of compounds of the type $MX_n(lp)_{4-n}$ with n = 2 or 3. The results of the correlations are reported in Table I. The van der Waals radii used were taken from Bondi's compilation with the exception of the values for Sb and for Bi. The value of r_V for Sb was calculated from the correlation equation obtained for X^1 = Me (set 152). Values of r_{VM} are given in Table II. Eight sets have been correlated with eq 15, all with significant results. Calculated and observed bond angles are compared in Table IV. When X = H, excellent agreement is obtained between calculated and observed angles for all M except O and N. The very large deviation obtained for O and N confirms the conclusion from the correlations with eq 8 that some factor or factors other than steric effects must be involved in determining these angles. Excellent agreement was also obtained for all M when X = Me, F, I, and 4-ZC_6H_4 (sets 152, 153, 157, and 161). In the latter case Z may be Me, I, H, or Br. No significant electrical effect of Z on the angle is detectable. When X is Cl (set 154) all M but S and Bi give very good agreement between calculated and observed angles. The deviation in the case of Bi is undoubtedly due to the large experimental error. That observed for S is in agreement with the results of the correlation with eq 8 for X_2S. The calculated

Table IV. Bond Angles and Deviations Obtained with Equation 15^c

set	X	M	O	N	P^a	As^a	S^a	
151	H	$\angle_{\text{obsd}}$	104.52	106.69	93.3(0.2)	91.83(0.33)	92.25	
		$\angle_{\text{calcd}}$	96.44	96.01	92.6	91.97	92.62	
		Δ	8.1	10.7	0.7	0.1	0.4	
			Se^a	Te^{a,b}				
			91.0(0.6)	89.5				
			91.3	89.4				
			0.3	0.1				
152	Me	As	N^a	P^a	O^a	S^a	Se^a	
		96(5)	110.6(0.6)	98.6	111.72(0.33)	98.90(0.2)	96.2(0.2)	
		97.4	110.3	99.2	111.82	99.23	95.6	
		1.4	0.3	0.6	0.1	0.3	0.6	
153	F		N^a	P^a	As^a	Sb^a	O^a	
			102.5(1.5)	97.8	96.1(0.2)	95.0	103.3	
			102.7	97.3	96.4	95.3	103.4	
			0.2	0.5	0.3	0.3	0.1	
154	Cl	S	N^a	P^a	As^a	Sb^a	O^a	Bi^b
		103	107.1(0.3)	100.3	98.4(0.5)	97.0	110.8(1.)	100(6)
		100.1	108.5	100.1	98.6	97.1	109.7	98.0
		2.9	1.4	0.2	0.2	0.1	1.1	2.0
155	CF_3	N^a	P	As^a	Sb^a	O^a		
		114(3)	97.2(0.7)	100.1(3.5)	100.0(3.5)	124.0(0.6)		
		117.8	103.0	100.6	98.3	120.0		
		3.8	5.8	0.5	1.7	4.0		
		S	Se					
		105.6(3)	97.0(2)					
		103.0	98.3					
		2.6	1.3					
156	Br	P	As	Sb^a	Bi^b	Te^b		
		101.5	99.66(0.26)	98.2	100(4)	98(3)		
		101.4	99.73	98.1	99.1	93.3		
		0.1	0.1	0.1	0.9	4.7		
157	I	P^a	As^a	Sb^a				
		102	100.2(0.4)	99.1(2)				
		101.9	100.4	99.0				
		0.1	0.2	0.1				
$(4\text{-}ZC_6H_4)_2M^b$								
161	Z, M	Me, S^a	Me, Se^a	Me, Te^a	I, O^a	H, N^a	Br, S	
		109(1.9)	106(2)	101(2.7)	118(3)	116(2)	109.5	
		108.6	105.8	101.6	117.9	116.8	108.6	
		0.4	0.2	0.6	0.1	0.8	0.9	

[a,b] See Table III. [c] Sources of all bond angles are reported in Table III unless otherwise noted.

angle from eq 8 is 98.3°, and from eq 15 is 100.1°. The observed value of 103.0° is inexplicably larger. When X = CF_3, a larger deviation than usual is the result. The largest deviation is for P. The angle calculated from both eq 8 and eq 15 for $P(CF_3)_3$ is 103.0°. We are unable to account for the very large discrepancy. Large deviations were also obtained for N and O. In the case of $N(CF_3)_3$ calculated values are 112.8 and 117.8° (from eq 8 and 15, respectively). Thus, the observed value lies between the calculated values. In the case of O, the values calculated from eq 8 and 15 are 120.5 and 120.0°, in very good agreement with each other. When X = Br, excellent agreement between calculated and observed bond angles is obtained except for Te. Since the experimental error is fairly large, this is not surprising.

From our results we can conclude that some other nonsteric factor (or perhaps factors) is responsible for the HMH angle when M is a second-period element. This factor cannot be repulsion between the comparatively unshielded H nuclei as the H-H distance should be about the same in all compounds which fit the model. A possible explanation is that, owing to the short MH bond length for M = O, N, and C, the electron density in the MH bond is much greater than in other MX bond lengths. Thus, for HOH, HNH, and HCH, electrostatic repulsion between bonding pairs would be greater than usual and could compete more effectively with lone pair-bond pair and lone pair-lone pair interactions.

The XMX angles in $MX_n(\text{lp})_{3-n}$ where $n = 2$ or 3 and X has the form WZ_3 with W = Si, Ge, and Sn are of considerable interest. When M = O or N, the angle is much larger than that calculated on the basis of steric effects alone. These angles are explicable in terms of $d\pi$-$p\pi$ bonding involving the lone pairs on N and O. The decreased electron density should result in a decreased repulsion betweeen the lone pair and bonding pairs. This would cause a larger angle. The large deviations observed for the PF_2 group in $O(PF_2)_2$ and $MeN(PF_2)_2$ are also in agreement with this argument. As expected, $CH_2(SiH_3)_2$ showed no significant deviation; large deviations were not observed for SX_2 with X = SiH_3, $SiMe_3$, or GeH_3. $Se(SiH_3)_2$ did not give a significant deviation. Large deviations were observed, however, for trisilyl- and trigermylphosphane and for trisilylarsane. In all cases, the observed angles are much smaller than the calculated angles. This could result from an increased electron density on the lone pair orbital on P or As. We cannot propose any reason for this to occur in the case of P and As but not in that of S or Se.

We have observed that PX_3 when X = OZ or NMe_2 and $S(NMe_2)_2$ show very large deviations. In all cases the observed angle is very much larger than the calculated angle. This phenomenon does not occur in $(Me_2N)_2SO$ or in X_3PY with X = 1-aziridinyl, Y = S, or X = OPh, Y = O. It does occur when X = OMe, Y = O. The failure of the steric model in PX_3 and SX_2 might be due to any combination of the following: (1) decreased electron density in the lone-pair orbital on P or S; (2) increased electron density in the PX or SX bond.

Table V. Results of Correlations with Equations 16, 17a, and 17b

set	slope	intercept	r^a	F^b	$s_{est}{}^d$	$s_{slope}{}^d$	$s_{int}{}^d$	$100r^2$ ^{d}	n^e
011	−0.714	1.577	0.8882	18.68[j]	0.0644	0.1651[j]	0.292[j]	78.88	7
011A	−0.389	0.976	0.9814	104.6	0.0111	0.0381	0.006 87	96.32	6
021	−0.660	0.688	0.8271	10.82[g]	0.0603	0.201[h]	0.122[j]	68.40	7
022	1.478	−0.0987	0.8802	17.19[j]	0.107	0.3571[j]	0.217[n]	77.47	7

[a-m] See Table 1. [n] 20% CL.

Although the central atoms which show this behavior have empty d orbitals available for π bonding, and the X groups involved have lone pairs capable of interacting with such orbitals, no clear connection between $d\pi$–$p\pi$ bonding and the observed deviations can be made. The P atoms in PF_3 also have d orbitals available for bonding, yet the observed angles fit the steric model very well. There is a third possible explanation, that $d\pi$–$p\pi$ bonding results in a change in the effective van der Waals radius of the OZ or NMe_2 group. Such π bonding would result in decreased rotation of the PX bond.

We have obtained values of a_1 and a_0 in another investigation. From these results we find $1/a_1 = 1.236(a_0/a_1) = 113.5$. From these results we predict that all of the correlations obtained with eq 8 should have an intercept of 1.236. In fact they are all in the range 0.872–1.211, in reasonable agreement with this prediction. When we attempt to calculate values of b_0 from eq 7a, we do not find agreement between the calculated values and those obtained from the correlations. Obviously some other factor is present. Equation 7a predicts a linear relationship between b_0 and r_{VM}. Thus, from eq 5a and 7a

$$b_0 = b_1 r_{VM} - 2(a_0/a_1) = b_1 r_{VM} + b_{11} \qquad (16)$$

Equation 16 is in fact obeyed. Results of the correlation are given in Table V (set 011). The results are improved by omission of the b_0 value for M = O (set 011A). Sets studied are 1, 2, 3, 13, 14, 15, and 16 with M = O, S, Se, N, P, As, and Sb, respectively. From eq 14 and 15

$$d_1 = b_1/r_{VX} \qquad (17a)$$

$$d_0 = b_0'/r_{VX} \qquad (17b)$$

and we predict linear relationships between d_1 and $1/r_{VX}$, and between d_0 and $1/r_{VX}$. Correlations with eq 17a and 17b give significant results. The statistics are reported in Table V (sets 021 and 022, respectively). The d_1 and d_0 values are from sets 151–157 with X = H, Me, F, Cl, CF_3, Br, and I, respectively. Our results may be summarized as follows:

1. Fourteen of the 15 sets correlated with eq 8 gave significant results. All of the eight sets correlated with eq 15 gave significant results. The b_0 values are correlated by eq 16; the d_1 and d_0 values by eq 17a and 17b. The b_1 values are in good agreement with the predicted value. It seems certain that, whereas the gross geometry of a classical species can be very well described by VSEPR theory, the actual bond angles are generally dependent on steric effects.

2. These conclusions have been demonstrated in tetrahedral and trigonal planar species. They are probably equally applicable to trigonal bipyramidal and octahedral species.

3. Substituents which can interact with a lone pair on the actual atom by $d\pi$–$p\pi$ bonding will not obey the steric model proposed here.

4. H atoms bonded to O, N, or C do not obey the steric effect model.

5. The van der Waals radii are satisfactory steric parameters for single-atom substituents. For polyatomic X, the group van der Waals radii are effective.

6. The correlation equations obtained permit the calculation of bond angles for a range of species of interest.

7. Bond angles measured by X-ray diffraction may show deviations resulting from the intermolecular forces in the crystal.

8. Coppens[10] has reported that in a system, YMX_2, where X is constant the angle XMX is a function of Y. This point supports our arguments as to the steric nature of the XMX angle. We will examine this type of system in the next paper of this series.

Acknowledgment. We would like to thank L. S. Bartell for pointing out the work of Coppens.

Supplementary Material Available: Results of correlations with eq 8 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Gillespie, R. J. *J. Am. Chem. Soc.* **1960,** *82,* 5978. (b) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: Princeton, N.J., 1972. (c) Gillespie, R. J. *J. Chem. Educ.* **1974,** *51,* 367.
(2) (a) Searcy, A. W. *J. Chem. Phys.* **1958,** *28,* 1237. (b) *Ibid.* **1959,** *31,* 1.
(3) (a) Bartell, L. S. *J. Chem. Phys.* **1960,** *32,* 827. (b) *J. Chem. Educ.* **1968,** *45,* 755. (c) Glidewell, C. *Inorg. Chim. Acta* **1975,** *12,* 219. (d) *Ibid.* **1976,** *20,* 113.
(4) Wilson, E. B., Jr. *Tetrahedron* **1962,** *17,* 191.
(5) Charton, M., unpublished results.
(6) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 263.
(7) Bondi, A. *J. Phys. Chem.* **1964,** *68,* 4441.
(8) Correlations were carried out by simple linear regression analysis. No attempt was made to weight the points in accord with the errors in the data.
(9) Charton, M. *J. Am. Chem. Soc.* **1969,** *91,* 615. *Prog. Phys. Org. Chem.* **1971,** *8,* 235.
(10) Coppens, P. *J. Chem. Phys.* **1962,** *36,* 2523.