Inorganica Chimica Acta, *164* (1989) 93–97

On the Steric Origin of Large Bond Angles in Siloxanes and Related Systems

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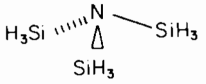
(Received January 27, 1989; revised May 26, 1989)

Abstract

The origin of the large XOX and XNX bond angles in molecules and ions containing polyatomic groups X headed by second (or later) row atoms, and/or in which the header atom W carries a substantial partial positive charge, is investigated by *ab initio* molecular orbital calculations. The widening of the angles is found to be due to steric clashes between the X groups which arise when the O–X bond lengths contract, rather than to arise from the requirements for bonding by the d orbitals. The effects do not occur unless the pi electron donor atom is drawn from the first row. The geometries of some XOOX and X_2NNX_2 systems are also discussed.

According to the simplest version of the VSEPR theory [1] and of the principles of directed valence [2], OX_2 and SX_2 molecules with univalent ligands X are expected to be strongly bent at the central oxygen or sulfur, and NX_3 and PX_3 molecules should be pyramidal at the central nitrogen or phosphorus. Indeed, the XOX and XNX angles in most such molecules fall in the 90°–110° range [1]. Well-known exceptions to these generalizations occur in OX_2 and NX_3 (but not SX_2 or PX_3) molecules when X is a polyatomic ligand headed by an atom W drawn from the second (or lower) row of the periodic table [1]. For example, the nitrogen in $N(SiH_3)_3$ (**1**) lies in the Si_3 plane, and the SiOSi angle in $O(SiH_3)_2$ (**2**) is 144° [3].



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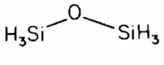

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Indeed most Si–O–Si, P–O–P, and S–O–S angles are significantly larger than 90°–110° [1]; see Fig. 1 for a summary of some illustrative experimental results. The driving force of such increases in XOX or NXN angle is often assumed to be the orbital overlap requirements of dative pi bonding between the lone pairs on the oxygen or nitrogen and the empty d orbitals on the second-row atom [1]. Alternatively, Glidewell has interpreted the structures of such compounds in terms of the steric requirements of the header atoms W [4]. Recently, we have shown that steric effects play a larger role in determining bond angles than generally suspected [5]. Here we show that the large XOX and XNX bond angles are due to X--X steric clashes, which are accentuated greatly by shortened OX and NX bonds. The bond contractions arise from partial ionic bonding as well as from the formation of partial double bonds.

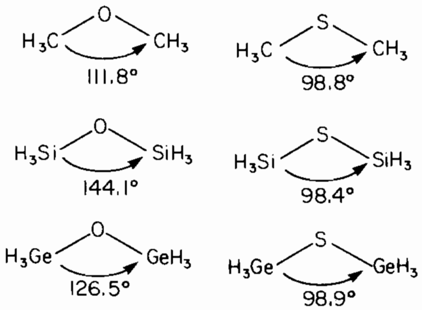

Fig. 1. Experimental bond angles [3] in XOX and XSX molecules.

All molecular orbital calculations discussed herein were executed using the GAUSSIAN86 computer program, and used the basis sets developed by Pople and his associates [6]. Except where specified to the contrary, the standard STO-3G basis set, supplemented as noted by d orbitals on second row atoms to become the STO-3G* basis, was employed. These bases are not the optimum bases to use in evaluating energies for small molecules containing first and second row atoms, but they have the advantage over the next higher levels† of sophistication (i.e. the 3-21G and 3-21G* bases) in that they do not

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†A referee has pointed out that because the silicon in siloxane is tetracoordinate and so positive, and because the oxygen there is so negative, it might be more appropriate to add d functions to O rather than to Si! The correct prediction of the Si–O–Si angle with larger basis sets apparently requires a correct balanced treatment of the ionic and covalent components. The STO-3G* basis set is probably not much superior to the STO-3G for present purposes, but it does show that our results are not artefacts arising from the neglect of d functions.

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consistently overestimate bond angles; in addition STO-3G calculations are sufficiently fast that even larger molecules, such as those containing CF_3 groups, can be handled. Within each ligand, the bond lengths and bond angles were usually fixed at standard values; tetrahedral angles were assumed within CH_3, CF_3, SiH_3 and SiF_3 groups, and the CH, CF, SiH and SiF bond lengths were assumed to be 1.09, 1.34, 1.48 and 1.57 Å respectively. One W–H or W–F bond within each unit was assumed to lie *trans* to the other O–X or S–X bond; the *cis,cis* orientation lies higher in energy and produces even larger XOX angles due to steric clashes between the in-plane H (or F) atoms.

As a prototype, consider the molecule $O(SiH_3)_2$. If we calculate the optimum Si–O–Si angle for an Si–O separation of 1.83 Å, which is the sum of the covalent single bond radii for the two elements, it is found to be 108.9° according to the calculation with d orbitals on the Si atoms, and 110.7° when the d orbitals are not included. (If the single bond distance of 1.749 Å extrapolated from the series ethane–methylsilane–dimethylether [7] instead is used, the calculated bond angles are 115°.) Indeed we find in general that bond angles in these exceptional XOX molecules do not increase much beyond the 90°–110° range provided that no bond length contraction is allowed, and we also find that the presence of d orbitals in the calculation at any particular distance has only a small effect on the angle. We have re-optimized the Si–O–Si angle for a variety of chosen SiO separations, as illustrated in Fig. 2. (The curve for the STO-3G results falls almost on top of that for STO-3G*, and for that reason is not shown. Detailed results are given in Table 1.) Clearly, the angle increases sharply as the SiO separation is decreased, in a manner similar to that found previously for AH_n and AF_n molecules and free radicals [5]. At the optimum STO-3G* separation of 1.583 Å, the optimum angle is 139.1°. If no d orbitals are included in the basis set, the predicted bond distance is longer, 1.656 Å, and consequently the angle is smaller, 124.1°. (Experimentally, the Si–O distance is 1.634 Å and the O–Si–O angle is 144° [3]. Unfortunately the next more sophisticated basis sets, 3-21G, 3-21G* and even 6-31G*, predict near linear Si–O–Si frameworks in this molecule, and so cannot be reliably employed in the present context. For other calculations on the prediction of geometry in siloxane, see ref. 8.) The calculated charges on the oxygen and silicon atoms are substantial: −0.60 e (−0.42 e) and +0.81 e (+0.59 e) respectively using the STO-3G (STO-3G*) basis at the optimum STO-3G geometry. The angle widens due to the steric repulsion between the silicon atoms, which is greatly increased due to the contraction of the SiO bond. This result is consistent with Glidewell's hypothesis [4]. O'Keeffe and Gibbs have noted that in the SiOSi system there is a charge density buildup interior to the SiOSi angle but a decrease in systems such as SiSSi and COC for which the angles are much smaller [8g]. As they point out, such correlations are not necessarily inconsistent with the notion that steric effects determine the angles.

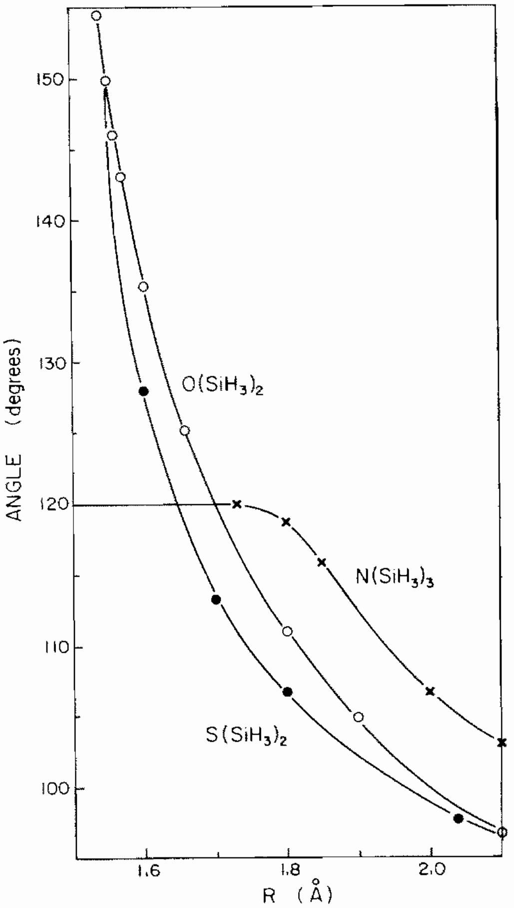


Fig. 2. Variation in calculated bond angle (by STO-3G*, except for 1 for which the STO-3G basis is used) with assumed Si–X bond length. (Angles for optimized bond lengths are shown in bold.)

Calculations (STO-3G*) for the optimum Si–S–Si bond angle in $S(SiH_3)_2$ (3) as a function of the Si–S separation are also shown in Fig. 2; the curve lies closer to that for the oxygen analog than do the corresponding ones for the simpler OX_2 and SX_2 systems considered previously [5a]. The experimental Si–S distance in $S(SiH_3)_2$ of 2.13 Å is not appreciably shorter than the value projected from analogs containing only single bonds [7], and the Si–S–Si angle is 98.4° [3]; the optimum STO-3G and STO-3G* structures have distances of 2.108 and 2.037 Å with angles of 100.7° and 97.7° respectively. Thus the angle in the sulfur analog is not enlarged; this contrast to the oxygen system occurs because the Si–S bonds are inherently longer, and because they undergo only

TABLE 1. Calculated bond angles

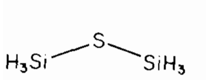
Molecule	R_{AW} (A)	Bond angle (°) calculated by	
		STO-3G	STO-3G*
1	1.50	120	
	1.60	120	
	1.70	120	
	1.734	120	
	1.80	118.7	
	1.85	115.8	
	2.00	106.6	
	2.10	103.1	
2	1.50		180
	1.54	150.0	154.6
	1.56		146.0
	1.57	139.5	142.8
	1.583		139.1
	1.60	132.7	135.2
	1.657	124.1	125.3
	1.80	112.3	111.0
	1.90	107.5	104.9
	2.10	100.9	96.8
3	1.55		150.3
	1.60	141.6	128.0
	1.70	120.4	113.2
	1.80	112.2	106.6
	1.92	106.3	
	2.037		97.7
	2.108	100.7	
	2.15		95.2
	2.21	98.6	
	2.30	97.2	
5	1.575	161.4	
6	1.25	128.7	
	1.30	123.7	
	1.33	121.1	
	1.369	118.2	
	1.415	115.2	
	1.50	110.7	

a negligible amount of contraction due to ionic character (the charges on Si and S are only +0.58 e and −0.25 e at the optimum STO-3G geometry) and to Si–S back bonding, compared to the appreciable contraction which occurs in the Si–O bond. The poor ability of sulfur, and indeed of all the second row elements, to act as electron donors in such bonding has been discussed previously by Schleyer and coworkers [9a]. Recently Schleyer has noted a correlation of the XOH bond angle with the electronegativity of X [9b]; since electronegativity correlates with the XO bond distance, this interpretation of the origin of bond widening is not inconsistent with our hypothesis.

As in $O(SiH_3)_2$, contraction in the bonds to oxygen occurs in $O(GeH_3)_2$ (4). The Ge–O length is not the 1.827 Å expected by analogy but rather is 1.766 Å [7]; the decrease amounts to about half that in the disilyl derivative. Since the Ge–O bond is inherently longer than is the Si–O, an expansion of the Ge–O–Ge angle only to 126.5° [7] is necessary to reduce the Ge–Ge steric clash. Given the small electronegativity difference between Ge and S, the poor ability of sulfur to act as an electron pair donor, and the large covalent radii of these two elements, little contraction in length and little expansion of angle is expected for $S(GeH_3)_2$; indeed the Ge–S distance is 2.209 Å (compared to 2.213 Å expected [7]) and the Ge–S–Ge angle is 98.9° [7].

The insensitivity of calculated bond angles to the presence or absence of d orbitals on second row atoms has been noted previously [6b]. Thus W–O–W angles do not open appreciably to provide a mechanism to delocalize the in-plane long pair on oxygen into d orbitals on the W atoms. Apparently the gain in energy associated with delocalizing the lone pair of electrons from a hybrid orbital of high 2p character on oxygen is effectively cancelled by the cost of promoting electron density from the s into that p orbital (i.e. to go from nominally a s^2p^1 configuration at 90° to a s^1p^2 configuration when the bond angle is 180°). As noted by other authors [8a], the energy required to linearize the Si–O–Si bond is small; for 2 at optimum STO-3G* geometries, we calculate it to be 1.2 kcal mol^{-1}. The energy to linearize becomes quite appreciable at uncontracted Si–O distances. (Small barriers to linearization of the P–O–P unit have also been noted [10]).

STO-3G calculations also have been performed on perfluorodisiloxane, $O(SiF_3)_2$ (5). The Si–O bond contracts by more than in disiloxane, to 1.575 Å calculated (compare to 1.58 Å experimental), and consequently the angle opens up further, to 161.4° calculated (compare to 156° experimental [3]). A linear Si–O–Si unit is found when the groups bonded to silicon are phenyl rings [11], which are very large. As mentioned briefly above, some of the O–W bond length contraction in these molecules is due to the delocalization of the oxygen lone pairs, principally that in a 2p orbital perpendicular to the WOW plane, into orbitals of the W–H or W–F bonds. This mechanism for stabilization (sometimes called 'negative hyperconjugation') leads to partial multiple bond character to the O–W link, and has been discussed in detail by Pople and Schleyer and their coworkers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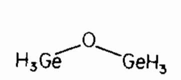
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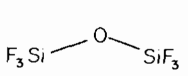
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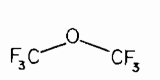
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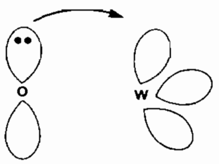
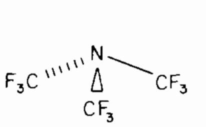
[6b, 12, 13]. The stabilization is greater the more polar are the bonds from W (with W the partially-positive end of each dipole). The donation of electron density from oxygen allows the bonds to become even more polar; formally this is achieved by the interaction of the bonding and antibonding MOs which is induced by the lone pair. When W is drawn from the second row (or lower) in the periodic table, this backbonding is supplemented by that from the oxygen lone pairs into the vacant valence-shell d orbitals.



In $N(SiH_3)_3$ (**1**) the lone pair on nitrogen can backbond into Si–H MOs and into 3d orbitals on silicon: this effect plus the partial ionic character of the Si–N bond should lead to a contraction in length of that link. Indeed the observed Si–N distance in this molecule is 1.734 Å [3], compared to 1.87 Å for the sum of the covalent radii of these two elements. Given the shortness of the bond and the consequent steric clash of silicon atoms, the Si–N–Si angles open up to 120° and produce a trigonal planar NSi_3 structure. According to STO-3G calculations, this geometry is optimal for Si–N distances less than about 1.75 Å; at longer separations, the repulsion of silicon atoms is sufficiently small that the geometry becomes pyramidal and the Si–N–Si angle falls to less than 120° (see Fig. 2). As expected, no significant opening of the Si–P–Si angle occurs in $P(SiH_3)_3$ (experimental value = 96.4° [3]).

Since bond contraction due to ionic character and at least a portion of the backbonding from O to W do not depend upon the availability of d orbitals, widening of the W–O–W angle should occur also when W is a first row atom of lesser electronegativity than oxygen if its bonds to its other ligands are quite polar (again with W as positive). Indeed, the C–O–C angle in $O(CF_3)_2$ (**6**) is observed to be 119.1°, compared to 111.8° in dimethylether, since the observed bond distance in the former of 1.369 Å is considerably shorter than the 1.415 Å in the latter [3]. In contrast, the C–S–C angle in $S(CF_3)_2$ of 97.3° differs only slightly from that of 98.8° in dimethylsulfide [3]. Similarly, in $N(CF_3)_3$ (**7**), the CN_3 framework is almost planar since the NCN angle is 117.9°; the CN distance here is 1.426 Å, compared to 1.458 Å with an angle of 110.9° in trimethylamine [3]. Again, the angle in the second row analog, $P(CF_3)_3$, is normal, 97.2° [3].



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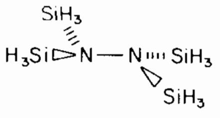

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In order to explore further the underlying mechanism for angle widening, STO-3G calculations have been performed on $O(CF_3)_2$ at a variety of O–C distances; the results are given in Table 1. At the optimum angle, the closest F- -F distance between fluorine atoms bonded to different carbon atoms is remarkably constant over a range of C–O values; it falls within 0.01 Å of 2.475 Å for a range of carbon–oxygen separations from 1.30 (with a bond angle of 123.7°) to 1.50 Å (with an angle of 110.7°). This is strong evidence that the bond angle in **6** is controlled by the steric clash of fluorine atoms. (Indeed if each trifluoromethyl group is rotated 60° so that the in-plane fluorine atoms are *cis* rather than *trans* to each other, the COC angle opens appreciably wider to reduce this short F- -F separation.) The closest H- -H separation in dimethylether does not remain quite as constant when the C–O length is varied as does the F- -F in **6**, but the variation still is small (2.315 Å when the CO length is 1.415 Å compared to 2.231 when it is 1.150 Å). When the CCH angles for the four out-of-plane H atoms were allowed to vary, they rose to 115.3° and thereby permitted the H- -H separations to increase to 2.480 Å when the CO distance was reduced to 1.15 Å. Thus it appears that XOX (and presumably XNX) angles are determined predominantly by steric clashes between atoms bonded to the header atoms when W is drawn from the first row (and hence is itself a small atom).

Corresponding calculations and analyses for molecules which contain a second (or later) row atom show that it is the steric clash between the W atoms themselves that determines the optimum angle there. For example the Si- -Si distance in $O(SiH_3)_2$ remains in the range from 2.93 to 2.99 Å as the Si–O distance varies from 1.80 to 1.54 Å and the Si–O–Si angle varies from 112° to 150° according to STO-3G calculations. (Glidewell deduced that the steric radius of silicon is 1.55 Å, in good agreement with one-half this separation [4].)

The steric clash of X ligands in OX_2 and NX_3 can be relieved further if an X group is replaced by one which forms a long bond with oxygen or nitrogen, and/or is itself a small atom. For example, in $(SiH_3)_2N{-}N(SiH_3)_2$ (**8**) the smallness of nitrogen atoms and the length (1.457 Å) of the N–N bond allow the Si–N–Si angles to increase to 129.7° (from 120° in $N(SiH_3)_3$). Similarly, the COO angle in CF_3OOCF_3 is 107.2°, compared to the COC angle of 119.1° in $O(CF_3)_2$ [3]. The O–F distance in HOF is longer, by 0.037 Å, than in F_2O; thus the bond angle of 97.2° in HOF is less than that of 103.1° in F_2O [3]. On the other hand, in F_2O_2 the O–O bond length is short and the F–O distances are long. Thus the FOO angle (109.5°) is significantly larger than the FOF angle (103.1° [3]) because such an OF group is larger sterically than is an F atom. In contrast, in N_2F_4 (9) the N–N bond is long (1.492 Å experimentally) and the FNF angles open up only very slightly (to 103.1°, from 102.4° in NF_3 [3]). Interestingly, *ab initio* MO calculations which force local planarity within each NF_2 group and a twisted geometry predict a substantial shortening of the NN bond (to 1.34 Å according to STO-3G results) due to donation from the purely p lone pair into the NF bonds, in analogy with the results for F_2O_2.

In conclusion, an analysis of both *ab initio* MO calculations and experimental structures suggest that the abnormally large W–O–W and W–N–W angles observed in many systems arise from the relief of steric clashes between the W atoms, or ligands bonded to them. The clashes occur because of the contraction of the W–O or W–N bonds which in turn arises from the partial ionic character of the bond and from back-bonding from the lone pair perpendicular to the WOW or WNW plane into polar MOs formed by W or into empty d orbitals on W. Consistent with this model is the general trend of bond angles observed [1] in polysiloxanes, polyphosphates, polysulfates, and polychlorates.

Si–O–Si > P–O–P > S–O–S > Cl–O–Cl

Here the ligands are groups headed by oxygen, the polarity of the bonds to which decreases in the order Si–O > P–O > S–O > Cl–O due to the electronegativity trend along this series, and so the extent of bond length contraction due to ionic character and back donation from the central oxygen will also decrease in this order.

Acknowledgements

The author is grateful to Professor B. M. Gimarc for suggesting this problem, to Professor C. J. Willis for useful discussions, to Toyanne M. Lauriston for assistance with the calculations, and to the Natural Sciences and Engineering Research Council of Canada for financial support.

References

1 R. J. Gillespie, *Molecular Geometry*, Van Nostrand Reinhold, London, 1972.
2 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.
3 J. H. Calloman, E. Hirota, T. Iijima, K. Kichitsu and W. J. Lafferety, *Structure Data of Free Polyatomic Molecules*, Springer, Berlin, 1987.
4 C. Glidewell, *Inorg. Chim. Acta, 12* (1975) 219.
5 (a) N. C. Baird, *Inorg. Chem., 28* (1989) 1224; (b) N. C. Baird, M. Kuhn and T. M. Lauriston, *Can. J. Chem.*, in press.
6 (a) W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986; (b) M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Martin, J. J. P. Stewart, F. Bobrowicz, D. Defrees, R. Seeger, R. Whiteside, D. Fox, E. Fluder and J. A. Pople, *GAUSSIAN86 (release C) program*, Carnegie-Mellon University, Pittsburg, 1986.
7 C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and S. Cradock, *J. Chem. Soc. A*, (1970) 315.
8 (a) G. V. Gibbs, E. P. Meagher, M. D. Newton and D. K. Swanson, in M. O'Keeffe and A. Navrotsky (eds.), *Structure and Bonding in Crystals*, Vol. 1, Academic Press, New York, 1981; (b) A. Tachibana, H. Fueno, Y. Kurosaki and T. Yamabe, *J. Am. Chem. Soc., 111* (1989) 806; (c) S. Grigoras and T. H. Lane, *J. Comp. Chem., 8* (1987) 84; (d) C. Glidewell and C. Thomson, *J. Comp. Chem., 3* (1982) 495; (e) C. A. Ernst, A. L. Allred, M. A. Ratner, M. D. Newton, G. V. Gibbs, J. W. Moskowitz and S. Topiol, *Chem. Phys. Lett., 81* (1981) 424; (f) G. V. Gibbs, P. D'Arco and M. B. Boisen, Jr., *J. Phys. Chem., 91* (1987) 5347; (g) M. O'Keeffe and G. V. Gibbs, *J. Phys. Chem., 89* (1985) 4574.
9 (a) P. v. R. Schleyer, E. D. Jemmis and G. W. Spitznagel, *J. Am. Chem. Soc., 107* (1985) 6393; (b) P. von R. Schleyer, *Pure Appl. Chem., 59* (1987) 1647.
10 C. S. Ewig and J. R. Van Wazer, *J. Am. Chem. Soc., 110* (1988) 79.
11 C. Glidewell and D. C. Liles, *Acta Crystallogr., Sect. B, 34* (1978) 124.
12 J. A. Pople, *Tetrahedron, 30* (1974) 1605.
13 P. v. R. Schleyer and A. J. Kos, *Tetrahedron, 39* (1983) 1141.