

Anomalous Geometry in μ -Oxo and μ -Nitrido Compounds of Silicon, Phosphorus, Sulphur, and their Heavier Congeners: Stereochemical Inactivity of Lone Pairs in the Presence of Ligands of Low Electronegativity

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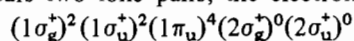
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In μ -oxo and μ -nitrido compounds of silicon, phosphorus, sulphur, and their heavier congeners of types $O(MR_n)_2$ and $N(MR_n)_3$, the inter-bond angles at oxygen and nitrogen are generally much larger than those predicted by the VSEPR model. The lower limiting values of the angles $\langle MOM$ and $\langle MNM$ can usually be predicted by a hard-atom model [1] but this model cannot account for the linearity at oxygen observed in, for example, certain disilicates [2], $O(SiPh_3)_2$ [3], $K_2Pb_2Ge_2O_7$ [4], and the β -phases of a number of diphosphates [5]; and the question naturally arises why these species should contain linear MOM fragments.

This question is most readily answered by reversing it and enquiring in turn why most oxo compounds $O(MR_n)_2$ (in which M is *p*-block element and *n* ranges from 0–3) are in fact non-linear at oxygen. Pearson has shown [6, 7] that the theoretical justification of the VSEPR model can be derived by the use of the second-order Jahn–Teller (SOJT) effect. In terms of the SOJT effect, any linear AX_2 species containing one or two (but not three) pairs of non bonding electrons localised in A will normally be unstable to bending; while an AX_3 species containing a single non-bonding pair localised on A will normally be unstable with respect to distortion along the out of plane bend (the umbrella vibration), giving a pyramidal skeleton.

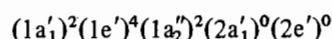
It must be emphasised that these conclusions are valid *only* when the valence shell orbitals of the ligand atom X are bound at least as tightly as those of the central atom A. When the ligand atom orbitals are less tightly bound (*i.e.* are less electronegative) than those of A, *no* distortion from linearity of AX_2 or from planarity of AX_3 is expected; and consequently the lone pair or pairs on A are stereochemically inactive.

Suppose for simplicity that in $A(MR_n)_2$, the central atom A contributes *ns* and *np* valence-shell orbitals, while the ligands MR_n each contribute a single σ -type orbital. Then for linear $A(MR_n)_2$ in which A bears two lone pairs, the electronic configuration is



The principal factor which determines whether the linear configuration is stable with respect to bending is the energy gap $I(1\pi_u) \leftrightarrow I(2\sigma_g^*)$: if this is large [6, 7], the system remains linear, but if it is small, distortion will occur along a vibration of symmetry $\Pi_u \times \Sigma_g^+ = \Pi_u$; that is, along the skeletal bending vibration. Since $1\pi_u$ is localised exclusively on the central atom, then the less tightly bound are the ligand orbitals relative to those of the central atom, the bigger will be the crucial gap between $1\pi_u$ and $2\sigma_g^+$, and the smaller the tendency of the skeleton to bend. Conversely, when the ligand σ orbitals are bound tighter than those of the central atom, the $(1\pi_u) - 2(\sigma_g^+)$ gap is small, so that the system bends along the Π_u vibration.

Similarly in $A(MR_n)_3$, using the same orbitals, the electronic configuration for a planar AM_3 skeleton bearing a lone pair on A is



Here the important energy gap is between $1a_2''$ and $2a_1'$: if this is small, as occurs when the ligand orbitals are the tighter bound, the system distorts along a vibration of symmetry $A_2'' \times A_1' = A_2''$; that is along the out of plane bend. However when the ligand orbitals are the less tightly bound, the $(1a_2'') - (2a_1')$ gap is large, and no distortion from planarity occurs. Hence the linearity of $O(MR_n)_2$ and the planarity of $N(MR_n)_3$ may be understood in solely electronic terms, provided only that MR_n is of low electronegativity.

It has previously been deduced [8] from the ionisation energies of compounds AH_n and $A(MH_3)_n$ (M = C, Si, Ge: A = Cl, Br, I; *n* = 1; A = O, S, Se; *n* = 2; A = N, P, As; *n* = 3: A = NCO, NCS, N_3 ; *n* = 1) that SiH_3 and GeH_3 are electron donors, rather than electron acceptors as has been generally supposed [9]. Similarly, it is scarcely conceivable that SiO_3^{2-} and GeO_3^{2-} are electron acceptors: in support of the view that they are electron donors, it may be noted that in species $O(MO_3)_2^{-2n}$ when M runs from Si (*n* = 3) through P and S to Cl (*n* = 0), as the electronegativity of $MO_3^{-(n-1)}$ increases and the $(1\pi_u) - (2\sigma_g^+)$ gap in the linear $O(MO_3)_2^{-2n}$ decreases, so also the inter-bond angle at oxygen steadily decreases, in each case limited by the $M \cdots M$ distance.

We wish to suggest that the anomalous geometries observed in μ -oxo and μ -nitrido compounds of silicon, phosphorus, and sulphur, and their heavier congeners are a consequence not of the electron acceptor properties of the MR_n groups *via* π donation from *p* orbitals of oxygen or nitrogen to *d* orbitals of M [9, 10], but rather of the electron donor properties of MR_n which substantially weaken the tendency of the linear $O(MR_n)_2$ and the planar $N(MR_n)_3$ to distort by means of the SOJT effect. The hard-atom contact distances $M \cdots M$ [1] are thus to be regarded not as

subtending an angle at oxygen or nitrogen which is expanded from its approximately tetrahedral VSEPR value, but as limiting the extent to which a weak bending force distorts a linear or planar molecule.

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