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GEOMETRY PREDICTIONS FOR π-BONDED MOLECULES USING SIMPLIFIED MO THEORY

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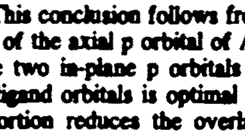
Abstract—A simplified version of Walsh's diagrams is proposed. Using this MO-based scheme, the angular geometry at dicoordinate and tricoordinate atoms in covalent molecules can be predicted, even when π bonding exists in the system. The basic "rule of thumb" developed is that distortion from the geometry of highest symmetry will occur only if the in-plane p orbital at the center of interest contains some antibonding, or appreciable nonbonding, electron density. These predictions are tested for a wide variety of molecules.

In the past, the prediction of molecular geometry by Molecular Orbital Theory using Walsh's rules and Mulliken–Walsh diagrams has been a somewhat complicated business, with many different diagrams and energy curves to be considered.[1,2] Recently it has been shown that, in fact, one master Walsh diagram serves for all AX_n (n = 2–7) systems (including hypervalent species) provided that no significant π bonding exists between the central atom A and the ligands X.[3] Here it is shown that the geometry for many organic molecules involving dicoordinate and tricoordinate C, N, etc. can be predicted and/or rationalized without recourse to complicated diagrams even when π bonding does exist in the system.

For any molecule of interest, consider first the "idealized" geometry which is defined as being linear at a dicoordinate atom and planar (with three approximately equal angles) for a tricoordinate atom. The problem is to predict whether a distortion will occur so as to transform the *linear* geometry to one which is *bent*, or the *planar* geometry to *pyramidal*:



Now such distortions will *not* occur if the only (valence-shell) electrons about the central atom are those which are involved in the two-center, two-electron σ bonds shown. This conclusion follows from the fact that the net overlap of the axial p orbital of A in linear AX_2, and that of the two in-plane p orbitals of A in planar AX_3, with the ligand orbitals is optimal in the idealized geometry. Distortion reduces the overlap and thereby weakens the single bonds; for reasons of symmetry and/or energy, the other p orbitals of A (unused for bonding in the idealized geometry) cannot be employed to compensate for the lost overlap. Since the overlap integral, and thus the strength of the bond, between the axial p orbital and the ligand orbitals in dicoordinate systems varies as the cosine of half the angle θ of distortion from linearity, a plot of bonding energy versus θ is quite flat near θ = 0° (linearity) but rises steeply for large θ (Fig. 1).† Thus for BeH_2 and other AX_2 species with only four electrons (all bonding) about A, the optimum geometry is linear and the bonding energy is harmonic in θ near the equilibrium angle.

As discussed previously,[3] distortion of the molecular geometry in an AX_3 system from ideality allows mixing to occur between an A–X antibonding MO (usually empty) and the p_π orbital perpendicular to the X_3 plane. Similarly, distortion from linearity allows mixing of an A–X antibonding MO with p_i, that p orbital which is *in* the plane of a bent AX_2 system. (The *out*-of-plane orbital, p_o, of bent AX_2 cannot mix with σ MOs under any conditions due to reasons of symmetry). One important effect of the mixing is to add s character to the p_i (or p_π) orbital, *thereby stabilizing the MO.* If the MO is nonbonding and is completely concentrated on A in the idealized geometry, this stabilization by acquisition of s content is the dominating effect and the orbital energy improves substantially upon distortion (Fig. 1). Thus the dihydrides such as CH_2 (singlet state) and NH_3 have geometries which are appreciably distorted from linearity and planarity, respectively,[3] because stabilization of the nonbonding electron pair by conversion of the purely p orbital to the s–p hybrid outweighs the loss in bonding energy of the A–H bonding orbitals when distortion from ideality occurs (Fig. 1).

The effect of geometric distortion upon MO stability is more complicated if the $p_{i(A)}$ orbital of an AX_2 molecule,

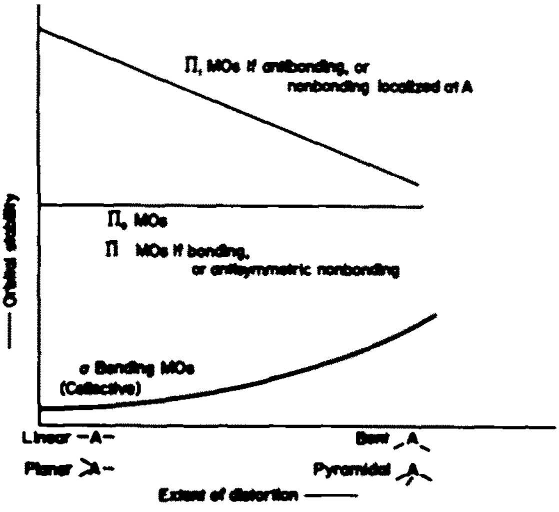


Fig. 1. Variation in orbital stability with geometric distortion.

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†Since cos X = 1 − X²/2! + X⁴/4! − ···, then for small θ/2, cos θ/2 varies as θ²/8.

or the $p_{\pi(A)}$ orbital of an AX_3, participates in π bonding with the ligands X. However, an analysis of Walsh's original diagrams,[1,2] of recent MO calculations, and of experimental structural results for many molecules of these types leads to some "rules of thumb" using which geometries can be predicted readily and fairly reliably. Thus it is postulated that *the stability of any MO which is A–X bonding is essentially unaffected by the distortion.* Two competing effects almost cancel to give this result. The MO gains stability by acquiring s_A character upon distorting, but loses a comparable amount of stability since the favourable A–X overlap of the (in-plane) π orbitals is thereby reduced.

Second, it is postulated that *nonbonding MO's which have nodal planes at atom A are also essentially unaffected in stability by the distortion.* The MO's of concern here are the antisymmetric in-plane MO (shown below) for a symmetrical AX_2 system and the two corresponding antisymmetrical π MO's of a symmetrical AX_3 system. Since contributions from orbitals of A are forbidden in such MO's, they can neither be stabilized by addition of s_A character nor destabilized by changes in A–X overlap upon geometric distortion. Similarly the MO's perpendicular to the plane in AX_2 molecules (i.e. the "out-of-plane" or π_0 MO's) are essentially unaffected in stability upon distortion since, by reason of symmetry, they neither add s_A character nor alter A–X overlap as a result.

Finally, it is postulated that *MO's which are A–X antibonding are sharply stabilized by the geometric distortion.* Such orbitals are stabilized both by the acquisition of s_A character and by the reduction in overlap of the p_i orbitals on A and the X's which gives rise to the antibonding.

A schematic representation of the effect of distortion upon the stabilities of these MO's is shown in Fig. 1. For AX_2 and AX_3 systems with π-bonding, the prediction of molecular geometry can be reduced to the simple rule that *only the presence of antibonding or nonbonding electron density in the p_i orbital* of an AX_2 molecule (or in the p_π orbital of an AX_3) *will cause the molecule to distort from its idealized geometry.*

The prediction that molecules in which all the π electrons are bonding in character should be linear at dicoordinate atoms and planar at tricoordinate atoms appears to be true and to apply to HAX, HAAH, H_2AA and H_2AAH_2 systems as well. Thus not only the well-known molecules $H{-}C{\equiv}N$ and $H{-}C{\equiv}C{-}H$ but also the more exotic species $H{-}C{\equiv}O^+$,[2] $H{-}\overset{+}{N}{\equiv}N$,[2] $H{-}N{=}C{:}$,[4b–5a] $H{-}C{\equiv}P$, $:C{=}C{=}C:$, and $H{-}C{\equiv}C{:}$[5] are all known† to be linear (or predicted by *ab initio* calculations to be so); the molecules $H_2C{=}O$ and $H_2C{=}CH_2$ are known to be planar and the species $H_2C{=}C{:}$ is predicted to be so.[5a]

Many examples exist of AB_2 molecules which have both bonding and nonbonding π electrons but in which

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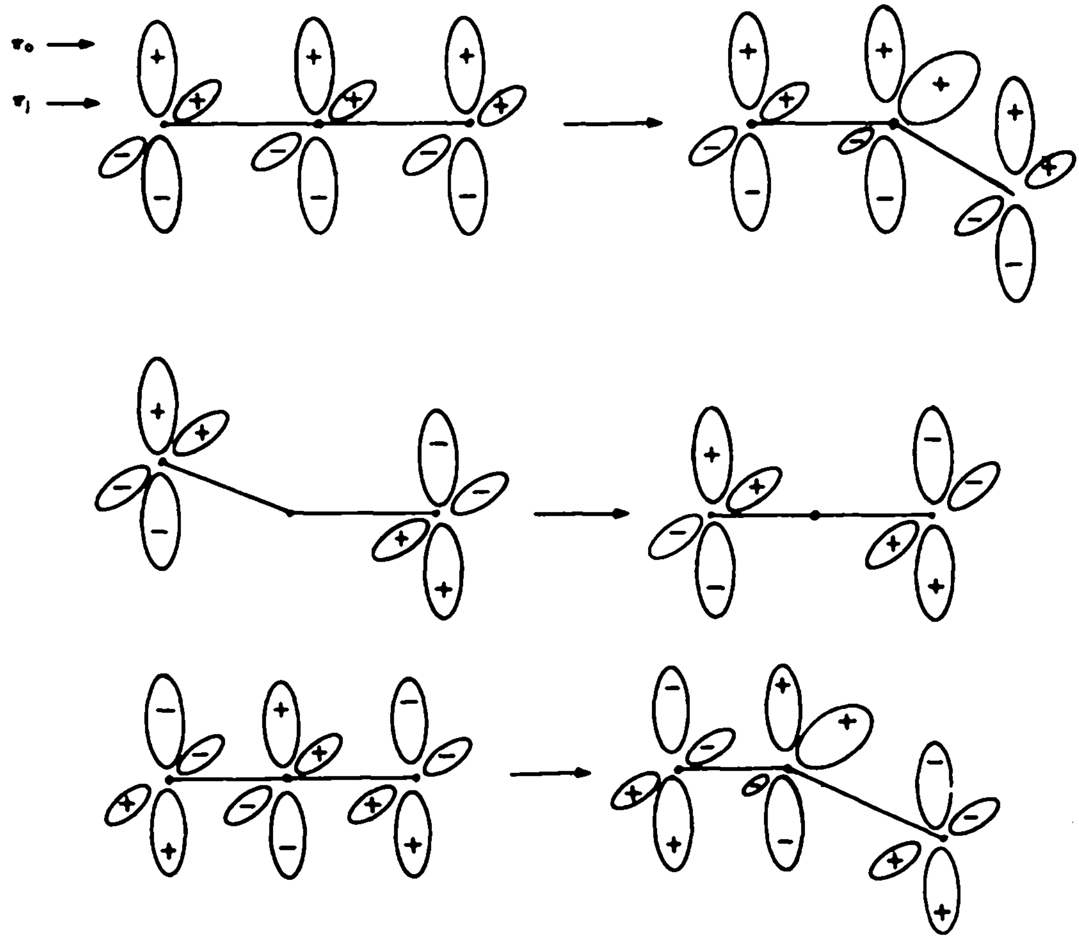
†Except as indicated to the contrary, all experimental structural information is from Appendix 6 of Ref. 4a.



the latter are symmetry-forbidden to be found at the central atom. As predicted, all possess the idealized geometry in their ground state; examples include the linear molecules N_3 and N_3^-,[1] CO_2 and CO_2^+, CS_2, CNC, NCN, and OBO. Linearity is also found for "YAX" systems in which the amount of nonbonding electron density in the p_t orbital of A is small either because the electronegativities of X and Y are similar (e.g. N_2O and N_2O^+, NCO, and CCN) or in which the electronegativity of Y is so high that its π electrons remain esentially localized on it and the electron density at A is almost completely bonding in nature (e.g. FCN(4*b*)). In the class of AX_3 systems with only π bonding density at A, the known examples (e.g. CO_3^{2-}, NO_3^-, BF_3) are planar[1] as predicted.

The addition of a further electron to NO_2 must result in antibonding electron density at the central atom, since both the in-plane and out-of-plane π bonding and nonbonding MO's are already all doubly-occupied. As expected, bending does occur; the angle in NO_2 is known to be 134°. The addition of yet another electron results in even more bending; the angles in NO_2^-, O_3, and SO_2 are 115°,[6] 117°, and 119° respectively. There exist also a number of HAX molecules with more than two electrons in one of the π systems and which therefore must have antibonding electron density at A; as predicted by extension of the AB_2 rules to these cases, all are bent. An example with one in-plane π^* electron is HCO at 125°,[7] and examples with two are the ground states of HNO (109°) and HCF (102°). Excitation of one in-plane π^* electron to the out-of-plane π^* MO results in excited states with larger angles for these two species (116° and 127° respectively) as expected. Excitation of the only in-plane π^* electron in HCO to the out-of-plane network yields a linear molecule, again as predicted. In contrast, excitation of an electron in CO_2 (or CS_2) must depopulate a nonbonding level and should result in a bent molecule if the excitation populates the in-plane π^* MO; such states of CO_2 and CS_2 are in fact known to be bent, with angles of ~122° and ~153° respectively.

The rules of AX_2 and HAX molecules can be extended also to HAAH dihydrides; these systems should be bent when the total number of inplane plus out-of-plane π electrons exceeds 4, but linear for 4 electrons or less. In agreement H–C≡C–H is linear but H–N=N–H[8] and H–O–O–H are strongly bent. The states of acetylene in which an electron is excited into the in-plane π^* MO are known to be bent, as required.

The rules concerning AX_3 systems apparently are generally valid also for H_2AX, HAX_2, H_2AAH and H_2AAH_2 molecules as well; thus pyramidalization is predicted and observed at the tricoordinate atoms in H_2HF[2] and H_2NNH_2, as well as in ClO_3 and ClO_3^-.[1] Excitation of one of the electrons of the oxygen atom lone pair into the π^*MO of formaldehyde should (and does) induce pyramidalization to occur at the carbon. Note that the stabilization by pyramidalization of a single *nonbonding* electron at a tricoordinate carbon is slightly *less* than the amount required do overcome the preference for planarity of the six bonding electrons, since the methyl radical is known to be weakly planar. The preference for "weakly pyramidal" geometries by the n, π^* excited states of H_2CO, and by the ground states of the H_2CF, HCF_2 and CF_3 free radicals[4b] suggests that the downward slope in Fig. 1 for the stabilization of a π^*MO should be somewhat more negative than for a nonbonding MO localized at atom A. This refinement in the postulates is consistent with the existence of two driving forces for stabilization of π^* orbitals (gain of s_A character and loss of antibonding overlap) as opposed to only one for nonbonding $p_t(A)$ or $p_\pi(A)$ orbitals; in addition it explains why the nonplanarity in fluoro derivatives of CH_3 increases with the number of fluorines.[4b] Note that the conversion of the nonbonding electron pair in NH_3 into a bonding pair via d_π–p_π bonding in $N(SiH_3)_3$ results in a coplanar arrangement of heavy atoms,[9] as predicted by the first postulate. Presumably the lone pair of the central atom in the carbanion $[C(NO_2)_2CN]^-$ is also bonding in character since this ion is planar.[10]

The extension of the present concepts to a discussion of the geometry in multiply-bonded HXYZ and like molecules requires that a stability line for the effect of nonbonded electron density at X atoms be deduced. (Presumably that for Y is identical to the one in AX_2 systems for antisymmetric nonbonding orbitals, provided X and Z are of similar electronegativity). Presumably the behavior of such an MO would be very similar to that for the nonbonding MO's in AH_2 and AH_3 systems, except that the downward slope of the stabilization line would not be as great since the lone pair density is shared between X and Z.

This consideration is adequate for molecules such as HN_3, HNCN, HNCO, HOCO and HONO since the electronegativities of the X and Z atoms are similar. In all four cases, substantial nonbonding or antibonding electron density is present at the atom bonded to hydrogen and sharp bending does occur.[11,12,4b] The electron density at the Y atom in HN_3,[11] HNCN and HNCO[12] should be almost entirely bonding in nature, and linearity there has not been questioned in structure studies for the parent molecules.† The chloro derivatives ClN_3[14] and ClNCO,[15] however, are both slightly bent at this position, presumably because contributions from $\overset{+}{\mathrm{Cl}}=\mathrm{N}-$ structures place nonbonding electron density at Y. As in NH_3, substitution of a silicon group for hydrogen in HNCO allows the nonbonding electrons at the nitrogen to acquire sufficient bonding character that Si–N–C angles of ~180° are preferred in H_3SiNCO[16] and in $(CH_3)_3SiNCO$.[17]

The two in-plane π^* electrons in nitrous acid, H–O–N=O cause sharp bending to occur at the nitrogen, as expected. Similarly H–O–C=O forms *cis* and *trans* isomers and must be bent at the carbon.[4b]

The rules discussed above are insufficient to predict the geometry of HXYZ systems in which the electronegativities of atoms X and Z differ substantially. Thus in the species HCNO one expects the π electron networks to be polarized toward oxygen so that structures **a**, **b** and **c** below should obviously be more important than is **d**, but since **a** prefers a linear geometry about carbon but **b** and **c** prefer a bent configuration, no "prediction" is made by this conclusion. Experimentally the H–C–N angle here is ~155°–170°[18] indicating that while **a** predominates, contributions from **b** and/or **c** cannot be ignored.

In the context of such molecules it is interesting that there exist a number of cyanides of the type R–C≡N in which the polyatomic group R possesses electrons which

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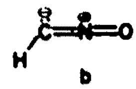
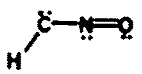
†See however the recent calculations in Ref. 13, in which slight bending at the Y atom in both HCNO and HNCO is predicted to occur.

a



b



c

d

could delocalize into the in-plane π system of the cyano group; in several cases a little bending at the carbon occurs, presumably due to a small build-up of nonbonding density there. Examples of this phenomenon are R = $-N_3$ (for which the angle is 176°[19]), –NO (172° ± 3°[20]), –SCN (175°[21]), $-PF_2$ (171° ± 3°[22]), and $-NF_2$ (169.7° ± 2.1°[22]). Note that, in the last two molecules listed, the R group is twisted so that the lone pair on P or N lies in the RCN plane, and therefore these electrons can interact with the in-plane π system of the cyanide group.

The ground state of HCCN is a triplet;[23] thus there are three electrons in both π systems. One contributing structure is the "carbene" form, $\mathrm{H{-}\dot{\underset{\cdot}{C}}{-}C{\equiv}N}$ for which a bent geometry at the H-bearing carbon is expected; in contrast, the "nitrene" structure $\mathrm{H{-}C{\equiv}C{-}\dot{N}}$ should prefer a linear geometry since there are no nonbonding electrons on carbon. Experimentally apparently a linear molecule is found,[23] and this is supported by sophisticated *ab initio* calculations.[24] The latter also predict that the CC and CN bonds are of lengths intermediate between those expected for the two extreme structures. Apparently for such a system the amount of nonbonding electron density at the H-bearing carbon is insufficient to bend the molecule.

Finally, the effect on their geometries of coordinating π-bonded molecules to transition metals should be noted. According to the qualitative theories, the ligands donate electron density from their π bonding MO's to the metal, and receive electron density into their antibonding π MO's from the metals d orbitals. The net effect to the geometry of the ligand should be dominated by the second factor, with the antibonding density inducing distortion from the idealized geometry. Examples here are the bending of acetylenes and the pyramidalization of ethylenes coordinated to metals in π-complexes.[25]

The combined experience of this paper and the previous one concerning the application of simplified Walsh diagrams to dicoordinate and tricoordinate atoms can be summarized as follows: The presence in a p_t orbital of –A–, or in the p_π orbital of –A, of any electron density which is A–X *antibonding* causes a geometric distortion to occur at A. In contrast, if the *only* type of electron density in such an orbital is bonding with respect to any of the ligands, no distortion occurs. Nonbonding electron density in substantial amounts in the orbital causes distortion to occur, although the density required for $-\mathrm{C}\!\!<$ (>1 electron) is larger than for –C–. In the latter context it is worth recalling[3] that the distorting effect of nonbonding electrons (i.e. the slope of the downward line) varies with the molecular charge and central atom type in the order

anions > neutral molecules > cations

and

3rd row atoms > 2nd row atoms.

Overall our view is not too dissimilar from that of Dewar who noted that most of Walsh's orbital diagram discussions may be summarized by saying that "placing electrons in antibonding orbitals is energetically unfavorable and leads to distortions".[26]

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