Systematics of the Molecular Geometry of Excited States and Free Radicals

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Abstract: The simple, noncalculational and nonempirical porous, blocked, σ-rich, π-rich method of structural fragments is extended to the prediction of the structure of excited states. This is directly applied to tri- and tetraatomic molecules (and then extended to larger species) by the simple rule: If one replaces a single unpaired electron with an electron pair, there is *no* interchange of the adjectives "porous" and "blocked." Justifications for the general validity of the suggested approach are also given.

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In a recent article,[1] we introduced the method of structural fragments as a nonempirical, noncalculational method of predicting molecular geometries. Application was made to the ground state of triatomic and tetraatomic molecules and ions. We now wish to show how extension can easily be made to the lowest lying excited state of these species. (Note that we will assume that the qualitative geometry description of the lowest lying excited singlet state is the same as that of the corresponding excited triplet state.[2,3]) First, however, let us briefly review the structural fragments procedure for predicting molecular geometries, in particular those of triatomic molecules. (Application to tetraatomic molecules requires but a simple extension.) We start by conceptually dissociating the triatomic molecule into atomic and diatomic fragments. The words "atom" and "molecule" frequently refer to charged species. We choose the diatomic fragment so that it is either isoelectronic with BH or CO, and so labeled σ-rich, or with HF or F_2, and so labeled π-rich. The atomic fragment, containing whatever electrons are left, is described as blocked if it has either a closed shell electron configuration or if it lacks but one electron of a closed shell configuration. If not blocked, the atom is labeled porous. Geometry predictions are made by applying the simple rules: σ-rich + porous → linear, σ-rich + block → bent, π-rich + porous → bent, π-rich + blocked → linear.

The object of this paper is to show that an analogous procedure may be applied to the qualitative geometry of excited state molecules. Quite surprisingly, in this study we find that we must often consider ground state atoms while the analogous study of the ground state molecules entails excited state atoms. For example, consider CO_2. By spin conservation and the Wigner–Wittmer rules,[4] ground state CO_2 cannot be dissociated into the ground state fragments $^1\Sigma$ CO and ^3P O. Instead, we must consider the ^1D state of atomic oxygen lying 45 kcal/mol above the ground state.[5] Conversely, the triplet excited state of CO_2 may be separated into ground state products. It is accordingly necessary to determine whether ground state atoms are porous or blocked. Noting the equivalence of a closed shell electron configuration and that of one electron short of a closed shell configuration in the definition of "blocked," the following simple rule is suggested. If one replaces a single unpaired electron by an electron pair there is no interchange of the adjectives "porous" or "blocked." This may be (in naive fashion) understood as both a closed shell σ-rich and π-rich diatomic fragment needing a two electron hole or pocket to form a two electron bond. The ^1D O may be written in

Lewis structures as Ö: whereas the corresponding picture for ^3P O is ·Ö· Therefore, ^3P O, ^4S N, and their isoelectronic analogs are blocked, while ^1D O, ^2D N, and their analogs are porous.

The reader will note that we do not discuss excited states involving ^2S H or ^2P F and their analogs. Since both σ- and π-rich diatomic molecules are closed shell by definition, we would be restricted to doublet excited states while our original intent would suggest quartet states. Our assumption that excited singlet S_1 and triplet T_1 states have similar geometries leads us to suggest that the excited doublet and quartet states will also have similar geometries. However, these species do not have corresponding excited quartet states. We will return to these species later.

The veracity of our assumptions is easily tested. We note that ^4S N and ^3P O are both blocked and thus both behave like either ^2P F or ^1S F$^-$. Admittedly artificially, we pair ^4S N and ^2P F, and ^3P O and ^1S F$^-$. The atoms in both pairs are interrelated by the second having two more electrons than the first. Accordingly, we deduce and thereby confirm Pearson's rule[2] that the geometry of the excited state triplet of a molecule with n electrons is the same as the ground state of the analogous molecule with $n + 2$ electrons. Pearson's success becomes our own. For example, the excited state of HCN is correctly deduced to be bent[3] since it is composed of the σ-rich HC$^+$ and blocked ^3P N$^-$ fragments. Although we had only spoken about triatomic molecules until now, the new structural awareness is easily extended to the assignments that $^4\Sigma$ CH, $^3\Sigma$ NH, and $^3\Sigma$ H$_2$ are all blocked by analogy to $^2\pi$ OH, $^1\Sigma$ HF, and $^1\Sigma$ H$_2^{2-}$. We thus find that the triplet state of HCCH, conceptually fragmented into the σ-rich HC$^+$ and the blocked $^3\Sigma$ HC$^-$, is nonlinear in agreement with experiment[3] and with Pearson[2].

We recall that ^2P B and ^3P C are both porous, as are ^2D N and ^1D O, while ^2S H and ^1S F$^-$ are blocked. A simple regularity is noted: an atom with an odd number of electrons has the same "porosity" as the neighboring atom to the right having an even number of electrons. This regularity persists in the comparison of the associated dihydrogen species: $^2\Sigma$ H$_2^+$ and $^1\Sigma$ H$_2$ are porous, while $^2\Sigma$ H$_2^-$ and $^1\Sigma$ H$_2^{2-}$ are blocked. Likewise, as also noted in ref 1, $^2\pi$ CH and $^1\Delta$ NH are porous while $^2\pi$ OH and $^1\Sigma$ HF are blocked. All of our σ-rich and π-rich diatomic molecules are by definition closed shell, and accordingly contain an even number of electrons. By our earlier geometry predictor based on the conceptual dichotomies of porous *vs.* blocked and σ rich *vs.* π rich, we conclude that triatomic or tetraatomic molecular species with an odd number of electrons have the same geometry as the related species with one more

Table I. Heats of Formation (kcal/mol) of NO, NO$_2$, HC, HCO, and Their Respective Cations[a]

X	XO	X	Diff	XO$^+$	X$^+$	Diff
ON	22	8	−14	235	234	−1
HC	−4	142	146	195	387	192

[a] "Diff" is not exactly equal to the X–O bond strength but may be directly related to it by adding the heat of formation of the appropriate state of atomic oxygen. The literature sources for the heats of formation of the NO$_2$$^+$, NO$^+$, HCO$^+$, and HC$^+$ ions are as follows: NO$_2$$^+$, V. H. Dibeler, J. A. Walker, and S. K. Winston, *J. Res. Nat. Bur. Stand., Sect. A*, 71, 371 (1967); NO$^+$, J. Unguin and E. Mitscher, *Can J. Phys.*, 47, 1769 (1969); HCO$^+$, C. S. Matthews and P. Warneck, *J. Chem. Phys.*, 51, 854 (1969), and HC$^+$, G. Herzberg, and J. W. C. Johns, *Astron. J.*, 158, 399 (1969). The heats of formation of the neutral species were obtained from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270–3 (1968).

electron. Elevating this conclusion to a general structural relationship, we find a useful complement to another of Pearson's rules.[2] He argues that the geometry of the excited state of a molecule with an odd number of electrons is the same as the ground state of the analogous molecule with one more electron. Our logic suggests the same prediction may be made for the ground state of such odd electron molecules. For the triatomic and tetraatomic molecules of this paper and references 1 through 3, only the isoelectronic cases of the planar CH$_3$ and NH$_3$$^+$ present themselves as exceptions while the bent HCO and NO$_2$ are in accord with this regularity.

Let us briefly consider some of the larger molecules presented in ref 2 and 3 and the general chemical literature. We note that Jahn-Teller distortion[6] of the odd-electron species is not built into our model. For example, the ground state of CH$_4$$^+$ is of nearly planar D_{2d} symmetry,[7] although we note that the trigonally distorted C_{3v} isomer lies only 3 kcal/mol higher in energy. Both structures may be simply related to the tetrahedral structure of CH$_4$[8] but we must admit our bias suggests the C_{3v} form of this ion. Since Jahn-Teller distortion is concurrent with the lifting of orbital degeneracies by reduction of the total molecular symmetry, we anticipate the regularities of interest will be most reliable for lower symmetry species. For example, we find both the ^2E ground state and the ^2A excited state of the odd electron CH$_3$O[9] are *essentially* pyramidal as is the even electron CH$_3$F.[3]

Let us now return to those excited state molecules that are fragmented into a σ- or π-rich diatomic molecule and ^2S H, ^2P F, $^2\Sigma$ H$_2$$^-$, or their isoelectronic analogs. For atomic hydrogen, there is no excited state without valence shell expansion. For atomic fluorine, there is an excited state not requiring such expansion, the s^{1}p^6 ^2S state. However, it lies over 80 kcal/mol above the ionization potential of the ground state s^{2}p^5 ^2P F (ref 5) and so may be disregarded for our purposes. Expansion is also not required for H$_2$$^-$ as there is the strongly antibonding σ^1 σ^{*2} $^2\Sigma$ state. We suspect that this similarly lies above the ionization potential of the ground state $^1\Sigma$ H$_2$. Admittedly using solely intuitive reasoning, we wish to argue that if the diatomic is strongly coupled to the H, F, or H$_2$$^-$ in the excited polyatomic molecule, then the bonding mimics the more strongly bound "cation" with one less electron. The extra electron is promoted and appears "free." Equivalently, the molecule may be described as being in a Rydberg state.

To test our hypothesis, we qualitatively consider the excited states of HCO and ONO which are fragmented into the σ-rich HC$^+$ and ON$^+$ and the blocked O$^-$. Experimentally, excited HCO is linear whereas excited ONO is bent.

We now attempt to reconcile this by considering the relative strengths of the C–O and N–O bonds in the ground state species HCO, HCO$^+$ and ONO, ONO$^+$. By spin conservation and the Wigner–Wittmer rules, neither HCO$^+$ nor ONO$^+$ may dissociate into ground state oxygen atoms, while the corresponding neutral species HCO and ONO may. However, for our purposes the exact state of the atomic oxygen fragment is irrelevant since both the neutrals and cations separately contain the same state. We thus need consider only the energy changes for the "reactions" XO to X and XO$^+$ to X$^+$ in which X = HC and ON. Table I presents the requisite thermochemical data and the relevant references. We find that the HCO$^+$ cation has a much stronger C–O bond than HCO, while ONO and ONO$^+$ have comparable N–O bond strengths. Using our previous argument concerning strongly bound atoms and the geometric similarity of the excited state and ground state minus an electron, we accordingly conclude that the excited state of HCO is more likely to be linear than ONO. We recall that the former is linear whereas the latter is bent[2,3] in qualitative agreement with our logic. We may simply explain the relative X–O bond strengths in the four species of interest using valence bond logic and drawing resonance structures. HCO has but one major resonance structure, HĊ=O, while HCO$^+$ has two, HC$^+$=O and HC≡O$^+$. Accordingly, the significantly greater bond strength in the cation is reasonable. In contrast, NO$_2$ has two equivalent resonance structures O=NȮ and ȮN=O while NO$_2$$^+$ would most probably be described as simply O=N$^+$=O. Accordingly, the increase of bond strength on loss of an electron from NO$_2$ would be expected to be small because of loss of resonance energy.

Our analysis provides no information as to the geometry of the excited state of CH$_3$. We note that it is indeed planar[2,3] as is the ground state but we also comment that CH$_3$ remains an enigma for qualitative predictions of molecular geometry. We now analyze the presented rules correlating species of different numbers of electrons in an attempt to understand both our success and failure. Following Berson and Salem[10] and Deb,[11] we will consider a modified Frontier molecular orbital model[12] and explicitly concern ourselves with the highest occupied orbital, ψ_{HOMO}, and the subjacent orbital, ψ_{SBMO}. The ground state of the n-electron (odd) species may thus be characterized by ψ_{SBMO}^2 ψ_{HOMO}^1 while the corresponding excited state is ψ_{SBMO}^1 ψ_{HOMO}^2. In constructing orbital energy and correlation diagrams, Walsh[13] assumed that their general "structure" depended solely on the number of atoms and not on the number of electrons. This suggests that the $n + 1$ electron (even) species should have the orbital configuration ψ_{SBMO}^2 ψ_{HOMO}^2. Whether or not ψ_{HOMO} dominates ψ_{SBMO}, we anticipate that ψ_{SBMO}^1 ψ_{HOMO}^2 and ψ_{SBMO}^2 ψ_{HOMO}^2 should yield the same geometry prediction. If ψ_{HOMO} is dominant, then when doubly occupied it will dominate ψ_{SBMO} whether that orbital is singly or doubly occupied. If ψ_{SBMO} is dominant, quite safely we may assume that ψ_{HOMO} is nonbonding. Therefore, the prediction is the same whether ψ_{SBMO} is singly or doubly occupied. Pearson's first rule is thus understood.[2] Analogous logic and indifference to dominance predicts that ψ_{SBMO}^1 ψ_{HOMO}^1 and ψ_{SBMO}^2 ψ_{HOMO}^2 should also correspond to the same geometry, thus explaining Pearson's second rule.[2] For our ground state odd electron rule to hold, we must assume that ψ_{SBMO}^2 is dominated by ψ_{HOMO}^1. The success of this rule suggests this assumption is usually valid. Moreover, we may now simply, although admittedly *a posteriori*, explain the general failure in predicting the planarity of CH$_3$ and NH$_3$$^+$. We recall that the inversion barrier for NH$_3$ is low (6 kcal/mol[14]). In the planar structure, the lone pair is a nonbonding π orbital and the

geometry is dominated by H–H antibonding interactions in the degenerate pair of subjacent orbitals (see Figure 1). We should not be surprised that $\psi_{SBMO}{}^4$ dominates $\psi_{HOMO}{}^1$ for the CH_3 and $NH_3{}^+$ radicals and indeed note that the nonplanarity of $SiH_3{}^{15}$ parallels the considerably higher inversion barrier for PH_3 (37 kcal/mol[16]).

The above delocalized molecular orbital logic can be mentally transformed back into bond pairs, lone pairs, and lone electrons. The former two "objects" are directly taken from Nyholm–Gillespie (valence shell electron pair repulsion[17]) logic. Lone electrons have not been invoked, but we note that application of this structural model to free radicals and excited states has almost never been made.[18] We predict that lone electrons should have the approximate stereochemical "size" of bond pairs. Bond pairs have two nuclei for two electrons while lone pairs have but one nucleus for two electrons. The 1:1 nucleus electron ratio applies for lone electrons as well as for bond pairs, thereby justifying our assertion. From strict size considerations, X–H should mimic X· better than any other bond, thereby generalizing the rule about the equivalence of the structures of phosphorus radicals and hydrides.[19] We further note that this is in accord with the correlation of $^2\Sigma$ CCF and linear HCCF vs. $^2\pi$ NCO and bent HNCO, as well as the prediction of the correct rotamer of HOOH from $^2A''$ HOO. (See ref 1 for discussion of the species and relevant literature citations.)

We may also formulate the geometry regularities of interest in terms of Takahata–Schnuelle–Parr (TSP) logic. We commence with an even electron species AH_mB_n, alternately written $A(H^-)_m(B^{b-})_n$ where by definition B^{b-} has a closed outer shell of electrons. Application of simple arithmetic shows that A has an even number of valence electrons left over (velo). In order for the molecule to have maximal symmetry, the number of velos must be zero or negative. Two velos distort the molecule while one velo, impossible here, would also cause distortion. One velo arises in the ground state of the related odd electron molecule with one electron less than the species with two velos. For example, $O_3 \equiv OO_2 \equiv O^{4+}(O^{2-})_2$ and $NO_2 \equiv N^{4+}(O^{2-})_2$ are indeed both bent.[2,3,20] Furthermore, since any nonpositive number of velos maintains maximal symmetry, the geometry predictions for velo = −1 and 0 are the same. For example, $BO_2 =$ "B^{4+}" $(O^{2-})_2$ and $CO_2 = C^{4+}(O^{2-})_2$ are both linear. We may again conclude that the ground state of an even electron molecule is the same as the corresponding odd electron molecule with one electron less. Excited states appear harder to describe; we will assume that these are charge transfer states. For example, the excited state of HOO may be described as $H^-O^{2+}O^-$, corresponding to $O_{terminal} \rightarrow O_{central}$ electron transfer from the ground state $H^-O^{3+}O^{2-}$. This charge distribution, analogous to $H^-O^{2+}F^-$ or HOF, is correctly predicted to be bent.[20] This procedure appears general: the excited state geometry mimics that species with the charge on the central atom reduced by one. This result is tautological to Pearson's rule[2] of the equivalence geometry of the excited state of an odd electron species with that of even electron species with one or more electron. Regretably, but not unexpectedly, the excited state of HCO is predicted to be bent. We may a posteriori argue that the excited state of $H^-C^{3+}O^{2-}$ is not $H^-C^{2+}O^-$ but $(H^-C^{4+}O^{2-})^+e^-$ in light of the strong CO bond in HCO^+ as discussed earlier in this paper. Insufficient evidence exists to justify this assertion.

Let us now consider excited states of even electron species. An analogous procedure applies. For example, the excited state of CH_2O may be written $(H^-)_2C^{3+}O^-$. We may deduce that this species is bent by nature of the central C^{3+} atom. (We are assuming that the planarity of CH_3 it-
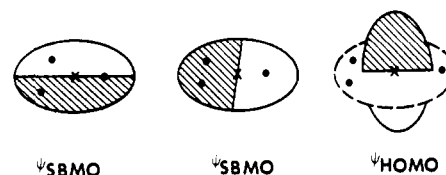

Figure 1. Orbitals for planar CH_3, $NH_3{}^+$, and NH_3: the • represents the hydrogen nucleus while the x represents the C or N nucleus. The crosshatched and clear parts of the diagram are used merely to represent the region of the respective wave function where the signs are + and −, respectively. All three functions have p like symmetry; indeed ψ_{HOMO} is almost purely ψ_{N2p} although it has a different orbital exponent or effective nuclear charge than in the free atom. By symmetry, there cannot be any contribution of the N 3d orbitals. We may use essentially the same pictures for the pyramidal form of the above trihydrides. N 3d orbital admixture is possible here since we have destroyed the plane of symmetry. Indeed, highly accurate quantum chemical calculations show that N 3d orbitals are required to obtain the pyramidal geometry of NH_3 (ref 14).

self is atypical of C^{3+} "containing" species.) This prediction is experimentally confirmed.[3] We additionally note that $(H^-)_2C^{3+}O^-$ would be expected to have a lower dipole moment than $(H^-)_2C^{4+}O^{2-}$. Indeed, the excited state of CH_2O has a dipole moment of 1.29 D (triplet) and 1.56 D (singlet) while the corresponding value for the ground state is 2.33 D.[21] Generalizing our procedure, we thus conclude that the geometry of the excited state of an even electron species is the same as the ground state of odd electron species with one more electron. (It is interesting to observe the equivalence of the geometry of excited n electron species and ground state n + 1 electron species is independent of whether n is odd or even.) Combining this relation with the first one above yields Pearson's second generality.[2]

In conclusion, the extension and application of the porous-blocked, σ, π-rich method of structural fragments to the excited state geometries of simple tri- and tetraatomic molecules is shown to be largely in agreement with experiment. The few exceptions can be justified by quite general arguments. Our method is consistent with the general and often extended rules of Pearson, Deb, Nyholm and Gillespie, and Takahata, Schnuelle, and Parr.

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Intramolecular Hydrogen Bonding in Monoanions of o-Phthalic Acid and the Homologous Oxalic Acid Series in Acetonitrile

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Abstract: First and second dissociation constants, K_1 and K_2. and homoconjugation constants, K_{homo}, of the homologous series of oxalic to azelaic acids, fumaric acid, and o-phthalic acid (H_2A), have been determined in acetonitrile. Also presented are the dissociation constant $K(HE)$ and homoconjugation constant $K(HE_2^-)$ of the corresponding mono methyl or ethyl esters (HE). Using these data and eq 1, the following values of $K' = [\overline{HA}^-]/[HA^-]$, $\overline{HA}^-$ denoting the intramolecular hydrogen-bonded species, have been found: malonic 2.5×10^4, succinic 5×10^3, glutaric 6×10^2, adipic 4×10^1, azelaic 1.5×10^1, o-phthalic 3×10^5. The intramolecular hydrogen bond in $\overline{HA}^-$ is quite stable, but the strength of this bond decreases with increasing distance between the carboxyl groups. No indication of $\overline{HA}^-$ species has been found in the monofumarate ion. In all of the above acids the homoconjugate $(\overline{HA}-H_2A)^-$ is present in excess over $(HA-H_2A)^-$, the ratio $[\overline{H_3A_2}^-]/[H_3A_2^-]$ decreasing as K' decreases. Evidence has been presented that the monoesters and the diacids are not intramolecularly hydrogen bonded in acetonitrile.

Hunter[1] attributed abnormally large ratios of the first to the second dissociation constants K_1/K_2 of many dicarboxylic acids, H_2A, to intramolecular hydrogen bonding in the monoanion, $\overline{HA}^-$. In accordance with this interpretation, Brown[2] stated that strain as a result of steric crowding of the carboxyl groups is relieved to some extent by formation of the intramolecularly hydrogen-bonded monoanion. Examples cited are alkyl-substituted succinic, malonic, and maleic acids. Very large values of K_1/K_2 have been obtained by Eberson[3] for rac-α,α'-dialkylsuccinic acids in 50% water-ethanol mixtures. A quantitative treatment of the effect of intramolecular hydrogen bonding in HA^- was given by Westheimer and Benfy.[4] They considered that in the familiar expression of K_1 the anion concentration is equal to $[HA^-] + [\overline{HA}^-]$, $[\overline{HA}^-]$ denoting the intramolecular hydrogen bonded form of the monoanion. They made the reasonable assumptions that the inductive effect of the carboxyl groups in the diacid H_2A and the carbalkoxyl group in the monoester HE are the same and that intramolecular hydrogen bonding in H_2A and HE is absent. Thus, for statistical reasons, K_1 should be equal to $2K(HE)$ in the absence of intramolecular hydrogen bonding in the monoanion. When there is intramolecular hydrogen bonding, relation 1 is easily derived. In eq 1, K' is the equilibrium

$$K' = [\overline{HA}^-]/[HA^-] = K_1/2K(HE) - 1 \qquad (1)$$

constant of the reaction $HA^- \rightleftarrows \overline{HA}^-$. From known values of K_1 and $K(HE)$ they concluded that in aqueous medium intramolecular hydrogen bonding between the carboxyl and carboxylate groups in HA^- is absent in the homologous series beginning with oxalic acid and in o-phthalic acid, since $K_1 \sim 2K(HE)$. In aqueous solution there is strong hydrogen bonding of the carboxylate and, to a much smaller extent,

of the carboxyl group to the solvent, thus stabilizing HA^- at the expense of $\overline{HA}^-$. Water is a much stronger base[5] and acid and also a stronger hydrogen bond acceptor and much stronger hydrogen bond donor than acetonitrile (AN). Hydrogen bonding of a carboxyl group with a dipolar protophobic solvent like AN is considerably weaker than that in water,[6] while the hydrogen bonding of the carboxylate ion with AN appears to be negligible.[6] Thus, it is to be expected that sizable values of K' in eq 1 may found in AN for o-phthalic acid and the homologous series of oxalic acid and that K' decreases with the number of $-CH_2-$ groups.

In the present paper are presented values of pK_1, pK_2, and $pK(HE)$ at 25° of oxalic, malonic, succinic, glutaric, adipic, azelaic, o-phthalic, and fumaric acids and their monomethyl or monoethyl esters in acetonitrile. Values of paH were determined potentiometrically with the glass electrode in mixtures of the diacids and their monotetraethylammonium salts and in mixtures of the mono- and ditetraethylammonium salts. To avoid decomposition of the tetraalkylammonium salts of the monoester acids, mixtures of HE and freshly prepared $\sim$1 M tetramethylammonium hydroxide solution in methanol were used. Correction was made for the effect on paH by the methanol thus introduced.

Homoconjugation constants have been calculated from paH values in mixtures of the diacid and its monoanion.[7] Considering that the monoanion is partly present as $\overline{HA}^-$ and partly as HA^-, and assuming that only the latter can intermolecularly hydrogen bond with H_2A to form the homoconjugate $H_3A_2^-$, expression 2 would be

$$K_{\text{homo}} = [H_3A_2^-]/([H_2A]([HA^-] + [\overline{HA}^-])) \qquad (2)$$

where K_{homo} is the observed homoconjugation constant. In the absence of intramolecular hydrogen bonding in HA