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Trends in Molecular Properties by the Method of Structural Fragments. Bond Angles in Triatomic Molecules, Pyramidal Inversion Barriers, and Singlet–Triplet Energy Differences

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Abstract: The recently suggested method of structural fragments is employed in this article to provide trends in bond angles, pyramidal inversion barriers, and singlet–triplet energy differences in carbenes and related electron-deficient species. No experiments or calculations need be performed. Instead, one merely counts the number of electrons in the appropriate fragments. Relative ionization potentials and electron affinities for the fragments are sometimes required, but intuition based on electronegativity trends usually suffices. The concepts of relative σ or π richness and of relative porosity or blockedness are thus introduced as natural extensions of the method described earlier. Analysis of the σ or π rich and porous or blocked fragment needed for reconstruction of the molecule then allows comparison of the species of interest with other compounds which are related either isoelectronically or by the loss or gain of electrons.

In two recent articles we introduced the method of structural fragments as a nonempirical, noncalculational procedure for predicting the molecular geometry of ground[2] and excited state[3] species. We now wish to show how this method may be employed to provide trends in bond angles, pyramidal inversion barriers, and singlet–triplet energy differences in carbenes and related electron-deficient species with no loss of generality or conceptual simplicity.

Let us briefly review the method of structural fragments as applied to the molecular geometry of ground state triatomic molecules. The triatomic molecule is mentally dissociated into diatomic and atomic fragments. The diatomic fragment is chosen to have either four or ten valence electrons and to therefore be isoelectronic with BH or CO, and to be labeled σ rich. Alternatively, if it has either eight or fourteen electrons and it is isoelectronic with HF or F_2, it is labeled π rich. In turn, if the remaining atomic fragment has a closed shell electron configuration or is but one electron short, it is labeled blocked; if not blocked, it is labeled porous. The geometry prediction is then made through the simple rules: σ rich + porous → linear, σ rich + blocked → bent, π rich + blocked → linear, π rich + porous → bent. For example, we recognize H^+ as porous but H and H^- as blocked. As such, we are not surprised that BeH_2, formed from the σ-rich BeH^- and porous H^+, is linear while BH_2, formed from the σ-rich BH and blocked H, is bent.[4] The lowest lying singlet state ($^1A_1$) of CH_2[5] is also bent since it may be fragmented into the σ-rich CH^+ and blocked H^-.

A seemingly reasonable rationalization of the above rules may be achieved by analyzing in greater detail the natures of the diatomic fragments. The so-called σ-rich fragments are of two types, which for generality will be denoted X–H and Y–Z. The X–H fragments contain four valence electrons and the Y–Z contain ten. For such numbers of valence electrons, the most generally probable Lewis structures are

$$:X:H \qquad \text{and} \qquad :Y:::Z:$$

both of which would be expected to involve sp hybridization. These structures suggest that both types of fragments should have very significant axial lone pairs, a conclusion supported by both theoretical and experimental studies. For example, the case of CO analysis of the electronic density distribution, as calculated from a near-Hartree–Fock molecular wave function, reveals highly localized lone pairs at both the carbon and the oxygen atoms.[6,7] The carbon lone pair is believed to play a key role in many CO interactions, such as its bonding to metals in metal carbonyls.[8] Taking BH as an example of a XH-type fragment, the presence of an axial lone pair on the boron has been confirmed by calculations showing that the degree of distortion of the boron atom in forming BH is greater than for the atom A in any other second- or third-row diatomic hydride AH.[9] An important part of this distortion is due to the increase of charge in the lone pair region, which is greater for BH than for any of the other hydrides.

Thus the crucial feature of the σ-rich fragments is that they possess important, highly localized lone pairs on the molecular axis. It is therefore to be expected that an electrophile, such as a "porous" atomic fragment, would find its most attractive path of approach to be along the axis toward the lone pair. For a nucleophile such as a "blocked" atomic fragment, this would, however, be the least attractive path; its preferred approach, if any, would be a nonlinear one. These deductions, which are statements of the first two rules given above, are supported by calculated molecular electrostatics potentials. For example, in N_2 the most negative electrostatic potential occurs at a point in the lone pair region and on the molecular axis.[10]

The π-rich fragments are also of two types, which will again be denoted X–H and Y–Z. They now contain eight and fourteen valence electrons, respectively. The most probable Lewis structures for these fragments are therefore

$$:\overset{..}{\underset{..}{X}}:H \qquad \text{and} \qquad :\overset{..}{\underset{..}{Y}}:\overset{..}{\underset{..}{Z}}:$$

Neither of these would be expected to involve hybridization to any significant degree. Accordingly it is not anticipated that either fragment will have highly localized and significant lone pairs. (Indeed, the fluorine in FH shows one of the lower degrees of distortion of the diatomic hydrides.[9]) Without lone pairs as a guide, it is not clear what path of approach would be most favorable for an electrophile or nucleophile. However, a reliable and understandable source of such information is the molecular electrostatic potential. This has recently been computed for FH;[11] it shows the most negative point to be near the fluorine, as expected, but *not* on the molecular axis. The point of most negative potential is at an angle of about 150° with respect to the F–H bond. This may be somewhat surprising, but it is certainly fully consistent with the rules we are trying to understand. Assuming that this situation is qualitatively the same for other π-rich fragments, this means that a porous atomic fragment being electrophilic would tend to approach nonlinearly (with respect to the X–H or Y–Z axis). A blocked atomic fragment then would either have to approach at almost a 90° angle to the axis or, seemingly more likely, along the axis. Thus we have arrived at the second pair of the four rules stated earlier. It should be emphasized that the preceding arguments are not being presented as a rigorous justification of these four empirical rules, but rather as a rationalization which does provide a qualitative basis for them.

We now turn to the first of the molecular properties for which we will derive trends by application of our rules.

Bond Angle Trends in Triatomic Molecules

In the introductory section we correctly predicted that BH_2 and $(^1A_1)CH_2$ are bent while BeH_2 is linear. We now wish to investigate bond angle trends in triatomic molecules in the framework of the method of structural fragments. For example, it is well established that the HAH angle in BH_2 is markedly larger than that of $(^1A_1)CH_2$ (131 and 102°, respectively). Likewise the ONO angle rapidly decreases in the order NO_2^+, NO_2, and NO_2^- (180, 134, 115°). We may explain both observations by introducing the concept of relative porosity and blockedness. Although we are not yet able to quantify this concept, we intuitively know that H^- is "less" porous (or "more" blocked) than H. Likewise H is "less" porous (or "more" blocked) than H^+. Thus CH_2, which can be fragmented into the σ-rich CH^+ and blocked H^-, would be expected to be "more" bent than BH_2, formed from the σ-rich BH and "less blocked" H. In turn, BH_2 is expected to be more bent than BeH_2. Since "more bent" is easily interpreted as having a smaller angle, we thus reproduce the qualitative geometry features of CH_2, BH_2, and BeH_2. Likewise, we interpret the decreasing ONO angle in the series NO_2^+, NO_2, and NO_2^- as a consequence of the conceptual fragmentation into the σ-rich NO^+ and the increasingly blocked O, O^-, and O^{2-}.

We are not limited to considerations involving σ-rich diatomic species. For example, the FClF angle increases in the order ClF_2^+, ClF_2 and ClF_2^- (95, 140, 180°)[12] in accordance with predictions made from combining the π-rich ClF with the increasingly blocked F^+, F, and F^-. The nonlinear geometry of ClF_2 violates the general geometry rules of the method of structural fragments[2,3] discussed above. However, XeF_2^+[13] and Cl_3[14] are isoelectronic to ClF_2 and yet are linear in accordance with the same rules. We may thus surmise that 21 electron triatomic molecules have low barriers to bending or structural deformation. This hypothesis is supported by the suggestion that facile geometry distortion in the noble gas fluoride radical cations, XeF_2^+, XeF_4^+, and XeF_6^+, may account for anomalies in the thermochemistry of the corresponding neutral molecules.[15] With regard to XeF_2^+, however, we will defer discussion of ease of bending of definitely *linear* molecules to a later publication.

Extension of the σ-Rich Class of Molecules and Pyramidal Inversion Barriers

Related inequalities may also be noted in the geometry of tetraatomic molecules. For example, H_2, H_2^-, and H_2^{2-} are decreasingly porous. We may thus deduce that CH_3^+, CH_3, and CH_3^- are increasingly pyramidal[16] as these species are fragmented into the σ-rich CH^+ and the above-mentioned "associated dihydrogen species",[2] H_2^{q-}. As we recall that the inversion barrier of CH_3^- is only ca. 5 kcal/mol,[17] we are not *too* surprised that CH_3 is planar,[18] an admitted exception to our rules. Alternatively, we could have compared BH_3, CH_3, and NH_3 and correctly concluded that these species are increasingly pyramidal, i.e., have increasing pyramidal inversion barriers.

We are clearly not limited to comparisons of only second-row elements. For example, the comparison of CH_3 and NH_3 is directly paralleled by the comparison of SiH_3 and PH_3. Indeed, from ref 3 we can justify the difference in the geometries of planar CH_3 and pyramidal SiH_3 by noting that the relative inversion barriers of the species with one more electron, NH_3 and PH_3, are ca. 6 and 37 kcal/mol, respectively.[17] Analogously, since O^- is more blocked than O, we conclude, correctly, that CH_2O^- is more pyramidal than CH_2O.[19] Likewise, assuming the closed shell F^- to be more blocked than O^-, NH_2F is predicted to be more pyramidal than NH_2O. Acknowledging the risk associated with comparing calculations at different levels of approximation, we note that NH_2O has been computed to be pyramidal with a barrier less than 1 kcal/mol[20] whereas NH_2F has been shown to have a barrier of at least 12 kcal/mol.[17] Experimental confirmation will prove difficult since substituted derivatives of NH_2O exhibit marked crystal and solvent effects on molecular structure[21] while most derivatives of NH_2F have strongly electron-withdrawing substituents.[22] Because F has a higher electronegativity than O^-, it is reasonable to believe F is more porous than O^-. From this, NH_2F^+ would be more planar than NH_2O. "More planar" in the case of NH_2F^+ implies planar since the inversion barrier of NH_2O is so low, and indeed quantum chemical calculations[23] suggest a planar geometry for NH_2F^+.

We additionally note that all of the above results are consistent with the hypothesis that the steric size of a lone electron is smaller than that of a lone pair.[3,24] As such, we have gained confidence in discussing free radicals not formally treated by the method of structural fragments.

Let us extend the method of structural fragments to include other types of σ-rich species. In the initial paper[2] which introduced this approach, HCN was suggested to be σ rich. We note that HCN and CO are isoelectronic, and so it appears reasonable to consider other polyatomic species which are isoelectronic with these two compounds. Using the term "isoelectronic" to mean the same number of valence electrons, such species include H_2CC and CH_3B. No surprises are expected with CH_3B as it is methyl-substituted HB. (CH_3C^+ and CH_3N^{2+} are likewise methyl-substituted HC^+ and HN^{2+}.) For example, from the knowledge that CH_3C^+ is σ rich and N^- porous, we may deduce that the C–C–N framework of CH_3CN is linear. Alternatively from the knowledge that HCN is linear and an awareness that small geometry changes accompany change of a C–H bond to a C–CH_3 bond in a molecule in general, we may immediately derive the same result. While this alternative derivation offers no surprise and no new information, if CH_3CN and HCN had had fundamentally different geometries, we would have had to revise numerous chemical concepts.

H_2CC and its analogues also behave in a manner consistent with our predictions. For example, H_2CC itself reacts with the porous H^+ to form the linear H_2CCH^+.[23] ("Linear" here means that the C–C–H framework is linear.) With the increasingly blocked H and H^- we find the increasingly bent vinyl radical and anion; vinyl radicals, although bent, are conformationally labile[25a] in contrast to the bent vinyl anions.[25b] Analogously, CH_2NH^+ has quantum chemically been predicted to be linear,[23] while the neutral CH_2NH has been experimentally shown to be bent.[26]

It would appear that extension of the class of σ-rich species is less ambiguous than that of π-rich species. The former class of compounds have but one electron donor site and essentially one acceptor site perpendicular to the donor. In contrast, donation from any, several, or all of the lone pairs of a π-rich species is in principle possible. Let us extend our list of σ-rich species to include CH_2, i.e., singlet methylene. This fragment naturally arises in a discussion of CH_3, $CH_3\cdot$, and CH_3^-, where the remaining atomic fragments are H^+, $H\cdot$, and H^-, respectively. With the porous H^+, we expect a "linear" product, while with the blocked H^- we expect a "bent" product (see Figure 1). "Linear" is thus seen to correspond to planar, while "bent" corresponds to pyramidal. Since the porosity of $H\cdot$ is intermediate between that of H^+ and H^-, we again conclude that CH_3^+ will be more pyramidal than CH_3^+ but less than CH_3^-. Equivalently, the inversion barrier of CH_3 may be anticipated to be less than that of CH_3^- in accord with experiment and our earlier discussion. Analogously, comparison of the porosity of O^- and F^- correctly shows that $NH_2^+ + O^- = NH_2O$ is less pyramidal than $NH_2^+ + F^- = NH_2F$.

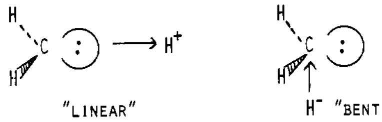

Figure 1. The σ-rich CH_2: combined with the porous H^+ and blocked H^- to form the "linear" (cf. planar) CH_3^+ and "bent" (cf. pyramidal) CH_3^-.

We may make comparisons even for species which are formally equally blocked or porous. For example, we may contrast NH_3 and NH_2F. Both species are clearly pyramidal as may be deduced from the fragmentation into the σ-rich NH_2^+ and the blocked anions H^- and F^-. The electronegativities of the atoms, H, N, and F, increase markedly in that order. As such, we surmise that $NH_2^+\ F^-$ contributes more to the wave function (i.e., is a more important valence bond or resonance structure) than $NH_2^+\ H^-$ to NH_3. Accordingly, NH_2F is predicted to be more pyramidal than NH_3 or essentially synonymously, the inversion barrier for NH_2F is predicted to be higher than for NH_3. Indeed, the general conclusion that inversion barriers for amines are increased by electron-withdrawing substitutes but decreased by electron-donating substituents[17] is understandable in terms of our logic.

We now briefly compare the inversion barriers of NH_3 and NF_3. By the earlier derived correlation of electronegativity of substituents and inversion barriers, the latter compound is predicted to have the higher barrier. Using the method of structural fragments we are to compare the resonance structures $NH_2^+\ H^-$ and $NF_2^+\ F^-$. From electronegativity logic, F^- is more "reasonable" than H^- since fluorine is more electronegative than hydrogen while NH_2^+ is more "reasonable" than NF_2^+ as fluorine is anticipated to destabilize cations. It thus seems we have to disentangle two opposing effects. However, this complication may easily be shown to be spurious. To form the ground state of pyramidal NH_3 and NF_3 from the appropriate molecular fragments, it is necessary to use the singlet ($^1A_1$) states of NH_2^+ and NF_2^+.[27] While this corresponds to the ground state for NF_2^+, it is an excited, i.e., higher energy, state of NH_2^+.[28] Furthermore, by application of the perfluoro effect,[29] we conclude that the π-ionization potential of NH_2 (yielding the desired ($^1A_1$)NH_2^+) is approximately equal to that of NF_2 (11.4[30a] and 11.6 eV,[30b] respectively). NF_2^+ and NH_2^+ are thus essentially equally "reasonable" and so $NF_2^+\ F^-$ contributes more to the NF_3 wave function than $NH_2^+\ H^-$ does to NH_3. It thus comes as no surprise that the inversion barrier for NF_3 is higher than that of NH_3.

Nothing we have said limits our treatment to amines and indeed the same trend has been shown for other AB_3 species such as carbanions, oxonium ions, silyl anions, phosphines, sulfonium ions and sulfoxides, and arsines.[17,31] We are aware of the warning of Mislow et al:[31b] "*any generalization assigning greater barrier magnitudes to all systems possessing an inversion center* ($MR^1R^2R^3$) *relative to corresponding systems possessing another inversion center* ($M'R^1R^2R^3$) *must be formulated with considerable caution.*" Let us nonetheless compare simple pyramidal species such as NH_3 and PH_3, H_3O^+ [24,32] and H_3S^+.[33] Analogous to our discussion of NH_3 and NH_2F, we may compare PH_3 with NH_3. Electronegativity reasoning suggests that $NH_2^+\ H^-$ contributes less to the NH_3 wave function than $PH_2^+\ H^-$ to PH_3. As such, we deduce, correctly, that PH_3 is more pyramidal than NH_3.[17,31] To compare H_3S^+ and H_3O^+, we may make a horizontal comparison from PH_3 and NH_3 and so understand the relative inversion barriers of these cations (30[17] or 35[33] kcal/mol and ca. 2 kcal/mol[32a]), respectively. Direct comparison of the electronegativities of O^+ and S^+ required for understanding the fragmentation of H_3O^+ and H_3S^+ into $H_2O^{2+} + H^-$ and $H_2S^{2+} + H^-$ gives the same trend. Admittedly although little is known about molecular dications,[34] it appears reasonable that $H_2O^{2+} + H^-$ will contribute less to the H_3O^+ wave function than $NH_2^+ + H^-$ to NH_3. We again conclude that NH_3 will have a higher inversion barrier than H_3O^+. Similarly, that of PH_3 will exceed that of H_3S^+ although we hesitate to compare structures formed from singly and doubly charged species.

We now wish to discuss alternate models of fragmentation of our AH_3 molecules of interest. In an earlier paper[2] we deduced that NH_3 and PH_3 were pyramidal as a consequence of fragmentation into the σ-rich NH^{2+} and PH^{2+} and blocked H_2^{2-}. By reasoning similar to our comparison of H_2O^{2+} and H_2S^{2+}, we may deduce that PH^{2+} is more "reasonable" than NH^{2+}. As such, PH_3 is again predicted to have a higher inversion barrier than NH_3. Data on dianions are even rarer than on dications. Nonetheless, let us consider the fragmentation of NH_3 and PH_3 into porous H_2^{2+} and π-rich NH^{2-} and PH^{2-}. From electronegativity logic, one might deduce that $NH^{2-} + H_2^{2+}$ is more favorable than $PH^{2-} + H_2^{2+}$ and so NH_3 should be more pyramidal than PH_3. However, one should not confuse electronegativity and electron affinity. From literature compendia of electron affinities,[35] we deduce that electron transfer from nitrogen to phosphorus is exothermic (cf. reactions 1–3).

$$N^- + P \rightarrow N + P^- \qquad (\text{ca. } 0.8 \text{ eV}) \tag{1}$$

$$NH^- + PH \rightarrow NH + PH^- \qquad (\text{ca. } 0.7 \text{ eV}) \tag{2}$$

$$NH_2^- + PH_2 \rightarrow NH_2 + PH_2^- \qquad (\text{ca. } 0.5 \text{ eV}) \tag{3}$$

Accordingly, we might anticipate that reaction 4, as written, is also exothermic.

$$NH^{2-} + PH \rightarrow NH + PH^{2-} \tag{4}$$

The exothermicity of reaction 4 can be rationalized in terms of the relative sizes of the nitrogen and phosphorus atoms. Since nitrogen is considerably smaller than phosphorus, the electronic charges in NH and NH^- must be much more concentrated than are those in the phosphorus analogues. The addition of another electron to the former is therefore opposed by particularly strong repulsive forces from the electrons already present. This interpretation is supported by the exothermicities of reactions 1–3. Similar effects involving the oxygen–sulfur pair[36] and the halogens[37] have been discussed previously. From the exothermicity of reaction 4, we thus conclude that PH^{2-} H_2^{2+} is a more important resonance structure for PH_3 than NH^{2-} H_2^{2+} is for NH_3, and so PH_3 has a higher inversion barrier than NH_3.

We may additionally understand our success in terms of Bent's rule:[38] "atomic p character concentrates in orbitals directed toward electronegative substituents", and his application of it to inversion barriers. The inversion barrier is maximized when there is a large electronegativity difference between the central atom and its substituents. The electronegativity difference between N and O is less than between N and F; accordingly NH_2^+ O^- contributes less to the NH_2O wave function than NH_2^+ F^- to NH_2F. Accordingly, by Bent's rule, NH_2O has a lower inversion barrier than NH_2F. Analogous considerations apply to all the other cases of pyramidal inversion barriers described in this paper. We thus find our approach is compatible with Bent's rule.

Singlet–Triplet Energy Difference in Carbenes and Related Electron-Deficient Species

In the preceding section of this article, we made note of the fact that NH_2^+ is a ground state triplet while NF_2^+ is a ground state singlet.[28] CH_2 and CF_2 are similarly ground state triplet and singlet species.[39] In contrast to CH_2, SiH_2 has a singlet ground state.[40] We will now try to understand the relative singlet–triplet energy difference in the above and similar species. Let us commence with a comparison of CH_2 and CHF, two particularly simple carbenes. Singlet CH_2 and CHF can be synthesized from the σ-rich CH^+ and the blocked H^- and F^- fragments, while the corresponding triplet species cannot be made from these same fragments.[27] From electronegativity considerations, CH^+F^- is a more important resonance structure for CHF than CH^+ H^- is for CH_2. Accordingly, CHF is more stabilized in the singlet state than CH_2. This logic may be directly applied to other CHX species with electronegative X.

In particular, let us consider X = NH_2 and OH. It might appear that $HCNH_2$, and other aminocarbenes, would favor the singlet less than HCOH, and other alkoxycarbenes, which in turn would favor the singlet less than CHF. This contradicts both experimental results on general carbenes[41] as well as literature quantum chemical calculations on the parent CHF, HCOH, and $HCNH_2$.[23] However, we recall FC^+ (cf. CO), HOC^+ (cf. HNC or HCN), and H_2NC^+ (cf. H_2CC) are σ rich and so in their interaction with the blocked H^- will yield bent, singlet carbenes. The importance of FC^+ H^-, HOC^+ H^-, and H_2NC^+ H^- in the carbene wave function is expected to increase in that order. As such, we should not be surprised that CHF, HCOH, and $HCNH_2$ are all ground state singlet carbenes. However, unfortunately, we cannot yet quantify the singlet–triplet energy differences for any of the molecules in this section, nor definitively determine if an arbitrary molecule is a ground state singlet or triplet.

Let us now consider disubstituted carbenes where X and Y are chosen from halo, alkoxy, and amino. Fragmentation into the σ-rich XC^+ and blocked Y^- correctly suggests bent singlets, although quantitation of the singlet–triplet energy difference evades us again.

Let us contrast CF_2 and the earlier mentioned CHF. Because fluorine should destabilize cationic carbon, FC^+ F^- might appear to be "poorer" than HC^+ F^- and thus CHF should favor being a singlet more than CF_2. This conclusion is false,[39] however, so we are forced to examine the reasoning. It may be shown that our fluorine-induced destabilization argument is fallacious on two grounds. First of all, fluorine directly attached to a cationic carbon is stabilizing relative to either hydrogen or chlorine,[42] but destabilizing further down the chain.[43] This conclusion is consistent with the perfluoro effect[29] which suggests that the π-ionization potentials of CH and CF are comparable (experimental values: 10.6[44a] and 9.2 eV,[44b] respectively). Second, we note that CF_2 has two equivalent resonance structures FC^+ F^- and F^- CF^+. An analogous case of two equivalent resonance structures has been suggested for noble gas difluorides[45a] with an accompanying resonance energy of 52 kcal/mol![45b]

Let us now turn to carbene analogues containing different central elements. Commencing with nitrenium ions,[46] NXY^+, we anticipate that for a given X and Y they will be more triplet than the corresponding carbenes since our intuition suggests NX^{2+} Y^- is a poorer resonance structure than CX^+ Y^-. Little comparable data exist,[41] but it appears that our prediction is valid. We earlier noted that SiH_2 is a singlet in contrast to CH_2. Using electronegativity logic we conclude that HSi^+ H^- contributes more to SiH_2 than does HC^+ H^- to CH_2. Since these structures can only apply to the singlet we thus understand the difference between CH_2 and SiH_2. What about phosphenium ions, PXY^+? We anticipate that these species will be "more" singlet than the corresponding NXY^+ ions but "less" singlet than SiXY from the electronegativity logic above. Reaction products of various alkyldichlorophosphines with olefins in the presence of $AlCl_3$ are suggestive of singlet $RPCl^+$

ions.[47] However, formally analogous reactions of sulfenyl chlorides do not proceed through RS^+ ions[48] and these may be anticipated to be ground-state triplets by analogy to HS^+.[49]

We had earlier mentioned nitrenium ions and so we may discuss nitrenes. In particular, let us consider aminonitrenes, R_2NN. In contrast to the isoelectronic carbonyl compounds, it has been suggested that these species are either ground-state triplets or else there is only a small singlet–triplet energy difference.[50] To explain this difference we fragment R_2NN into the σ-rich $(^1A_1)R_2N^+$ ion and porous $(^1D)N^-$ ion and R_2CO into the analogous states of R_2C and O. R_2N^+ is expected to be a poorer donor, i.e., be less σ rich, than R_2C because of its positive charge and N^- is expected to be less porous than O because of its negative charge. As such, R_2NN is more poorly represented by R_2N^+ N^- than R_2CO is by R_2C O. A more reasonable structure for R_2NN would arise from a combination of R_2N and N. Since these fragments are respectively a doublet and quartet, they may not form a singlet product. Instead, a triplet seems more likely. In addition, R_2C^+ O^- is another contributor to R_2CO and so corroborates the customary assumption of positive carbon in carbonyl compounds.[51] To have negative carbon requires participation of R_2C^- O^+ (doublet + quartet) and so might be expected in the excited triplet state. Experimentally,[52] it is found that the dipole moment of excited state CH_2O is markedly reduced from the ground state in accordance with our intuition.

We will conclude this paper by considering the O_2 molecule, which has the same number of valence electrons as R_2CO and R_2NN. The covalent resonance structure O O gives no information as to the multiplicity of the diatomic of interest. However, the ionic resonance structure O^+ O^- implies a triplet ground state. We remind the reader that because O_2 is a homonuclear diatomic molecule the contribution of O^+ O^- and O^- O^+ must be equal but need *not* be zero.

Conclusion

In conclusion we have found that the method of structural fragments provides a simple, noncalculational, and nonempirical procedure for deriving trends in bond angles, pyramidal inversion barriers, and singlet–triplet energy differences. While it has been necessary to extend some of the basic vocabulary of this method with new systems, no artifice or ambiguity arises to mar the generality or conceptual simplicity of the original approach.

Acknowledgment. J. F. L. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. W. A. S. thanks the donors of the Chemical Fund of the Department of Chemistry at the Catholic University of America for partial support of this work. J. F. L. would also like to thank Dr. B. M. Gimarc for his helpful comments and for his hospitality at the University of South Carolina where this research was finalized. Finally, the authors wish to thank Deborah Van Vechten for her editorial suggestions.

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