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Why Metalloid-Substituted Unsaturated Compounds Are Colored

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Abstract: A formal analogy between the lowest unoccupied molecular orbital (LUMO) of disilacyclopropanones, $(R_2Si)_2C{=}O$, and disilacyclopropanimines, $(R_2Si)_2C{=}NR'$, and a previously proposed model for the LUMO's of cyclopolysilanes, $(R_2Si)_n$, is observed and rationalized using simple MO concepts. The form of the LUMO is indicative of a large negative-hyperconjugative stabilization of chromophore antibonding orbitals and suggests that excited-state geometries of sila-substituted ketones and imines will be more nearly like their corresponding ground-state geometries than are those of alkyl ketones or imines. Thus one reason (heretofore unrecognized) that sila-substituted unsaturated compounds have longer wavelength UV absorptions is that their vertical excitation energies are more nearly equal to their adiabatic excitation energies.

Whereas the aliphatic and aromatic ketones, $RR'C{=}O$, are colorless compounds exhibiting broad, weak, structureless n → π* transitions in solution, the silicon-substituted ketones are colored compounds with more intense, structured, electronic transitions.[1-8] [In this paper, we are referring specifically to compounds in which silicon, or more generally a metalloid, is directly attached to an unsaturated center. Compounds such as $(R_3Si)R'C{=}O$ may be properly called sila-ketones, acylsilanes, or, more generally, acyl metalloids.] Explanations for the precipitous drop in excitation energy (by as much as 2 eV) upon substitution of carbon by silicon in the ketones initially focused on the role of silicon d-orbital stabilization of the excited state[3,4] and inductive destabilization of the oxygen lone pair by the relatively electropositive silyl groups.[5,6] Later studies employing photoelectron spectroscopy and CNDO/2 calculations have shown, however, that strong mixing between localized lone pair orbitals, n, and metal–carbon bonds, σ, is the main reason for the observed shifts and increased structure in the UV spectra.[7] Thus Ramsey, Brook, Bassindale, and Bock (RBBB) have argued that the longest wavelength transitions in the acylsilanes are better regarded as σ → π* than n → π* excitations.[7]

Within a molecular orbital framework, of course, excitation energies are dependent on both ground-state occupied and unoccupied orbital energies, and while RBBB have identified higher lying occupied orbitals as the principal reason for the large UV bathochromic shift upon sila-substitution, evidence exists for stabilization of unoccupied orbitals as well. In particular, Bock, Alt, and Seidl (BAS)[8] have measured half-wave reduction potentials (which are linearly correlated with the energies of the lowest vacant orbitals) of various mono-sila-ketones and found stabilization in the lowest antibonding molecular orbitals of about 0.2 to 0.3 eV. Therefore, both higher lying occupied *and* lower lying unoccupied orbitals are responsible for the large bathochromic shift in the UV spectra of ketones upon sila-substitution.

Our interest in this problem was fueled by the recent synthesis of the first disilacyclopropanimine ($(R_2Si)_2C{=}NR'$) by Yokelson, Millevolte, Haller, and West.[9] While mono-substituted C-silanimines had previously been synthesized and characterized by Brook, Golino, and Matern,[10] this represented the first case in which the sila-chromophore had been encased in a ring and presented interesting structural questions as well. Determination of the ground-state equilibrium geometries of the parent disilacyclopropanimine and disilacyclopropanone using standard self-consistent-field techniques, and subsequent inspection of the molecular orbitals, revealed that the lowest unoccupied molecular orbital (LUMO) was, in both cases, of the form indicated in Figure 1a for disilacyclopropanone. That is, it is a π-type orbital, antibonding between C and O as we expect, but also bonding between carbon and the two silicons, and antibonding between the silicons and the attached hydrogens.

This orbital is no stranger to us, as it is of the exact same form (i.e., completely ring bonding, exocyclic antibonding) as the one we found to be the LUMO in a previous study of the three-, four- and five-membered cyclopolysilanes, an example of which is shown in Figure 1b for cyclotrisilane.[11] We noted that a LUMO of this type could explain, simply by symmetry arguments, the small extinction coefficients for the longest wavelength UV absorptions of the experimentally known, heavily substituted, cyclopolysilanes.[12] Furthermore, it could easily account, once again by symmetry, for the observed ESR data on cyclopolysilane anion radicals which suggested little or no participation of silicon s orbitals in their singly occupied molecular orbital (SOMO).[12,13] It seemed at odds, however, with the results of recent ^{29}Si ENDOR studies[14] which suggested a small hyperfine anisotropy for ^{29}Si. To accomodate the ENDOR results, Wadsworth and West proposed a σ* model for the SOMO of the anion radicals,[15] but that model provides no obvious interpretation of the UV or ESR data.[11]

Given the seeming universality of this LUMO, we were compelled to seek justification for its presence. Proving that the LUMO in these systems will always be of this type is impossible, but we can show that an orbital of this type will be the π-LUMO, i.e., will be the lowest unoccupied MO that has a node in the plane of the heavy atoms. Of course, for molecules like the substituted ketones and imines, the LUMO is almost certainly of π* (C–O) or π* (C–N) type, and thus the following analysis will strongly suggest that the overall LUMO, not just the π-LUMO, is of the prescribed form.

Consider the out-of-plane orbitals that can be generated from a minimal basis set description of disilacyclopropanone in its ground-state equilibrium geometry of C_{2v} symmetry. They are only six in number: four of b_1 and two of a_2 symmetry. We may safely consider only the orbitals of b_1 symmetry because (a) the

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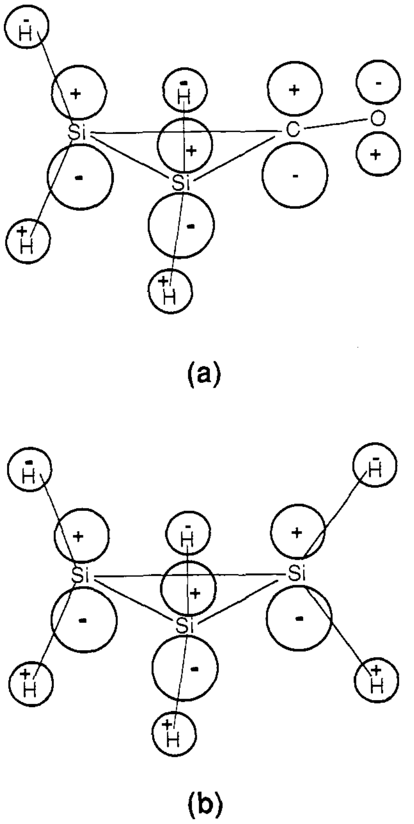

Figure 1. The lowest unoccupied molecular orbital (LUMO) in (a) disilacyclopropanone $(H_2Si)_2CO$ and (b) cyclotrisilane $(H_2Si)_3$. The silicon 3p orbitals are represented as 2p orbitals for clarity.

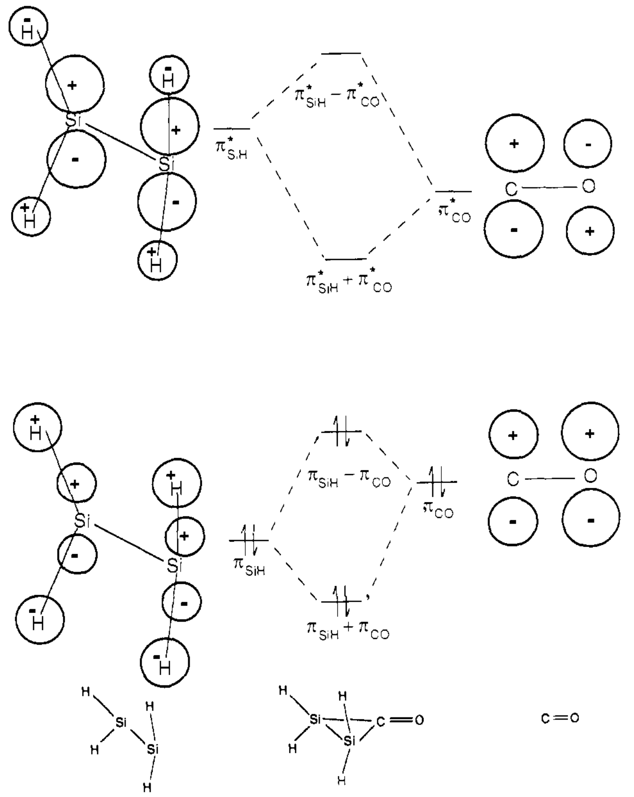

Figure 2. The b_1 symmetry π orbitals of disilacyclopropanone constructed from fragment π_{SiH} and π_{CO} bonding and antibonding orbitals. The silicon 3p orbitals are represented as 2p orbitals for clarity.

a_2 orbitals are of the wrong symmetry to mix with, and thus stabilize, a π* (C–O) orbital; and (b) the unoccupied a_2 orbital (one of them is doubly occupied) is highly nodal in character, being both Si–H *and* Si–Si antibonding. The four semilocalized symmetrized fragment orbitals of b_1 symmetry are shown in Figure 2. The bonding π_{SiH} and antibonding π^*_{SiH} orbitals are shown on the left and the bonding π_{CO} and antibonding π^*_{CO} orbitals are shown on the right.

By taking appropriate linear combinations of the bonding and antibonding fragment orbitals, we find the molecular orbital diagram in Figure 2. The lowest two of these are doubly occupied in the ground state. The lowest lying of the two antibonding π-molecular orbitals will be that linear combination of fragment orbitals that introduces the fewest nodes, $\pi^*_{SiH} + \pi^*_{CO}$, and we immediately recognize this as being identical with the orbital we actually found as the LUMO for disilacyclopropanone, disilacyclopropanimine, and the cyclopolysilanes (see Figure 1).

We could just as easily derive the preceding result by noting that, having excluded orbitals of a_2 symmetry from our analysis (and thus not allowing for any nodes between the silicons), the problem before us is really isomorphic to the problem of determining the form of the π orbitals in butadiene.[16] In both problems we have four atoms linked together (here we have H bonded to Si bonded to C bonded to O; in butadiene we have four carbon atoms bonded in a chain), and the resulting MO ordering is strictly determined by the number of nodes. The lowest lying MO has no nodes. The next MO has one node between the second and third atoms. The third MO has nodes between atoms one and two *and* between atoms three and four but is nodeless between atoms two and three, *just as we have here.* Finally, the highest lying MO has nodes between all the connected atoms (cf. Figure 2).

Since the form of the π-LUMO is determined only by the topology of these molecular systems, and not by the particular substituents attached to the carbonyl carbon, this must be the π-LUMO for cyclopropanone as well as for disilacyclopropanone. The crucial difference between silaketones and alkyl ketones is that with silaketones the occupied Si–H bonding orbitals are strongly polarized toward the more electronegative hydrogens, implying that the unoccupied orbitals (which are lower lying in the first place) will be predominantly silicon in character, and thus will overlap (and hence interact, in a negative-hyperconjugative fashion) more strongly with the π* orbital on the carbonyl group. This reasoning is identical with that used in explaining the dramatic stabilization of carbanions by α-silyl groups.[17]

Geometries of ground and excited electronic states are rarely the same. Knowledge of the type of MO's from which we are removing electrons and of those in which we are placing them in the excitation process often times allows us to make simple qualitative predictions about geometrical distortions that accompany light absorption. In the case of formaldehyde, $H_2C{=}O$, the lowest lying n → π* excitation removes an electron from a nonbonding orbital on oxygen, and places it in a CO antibonding orbital that is mainly of carbon p-character. Thus it is not surprising that the excited-state geometry has a significantly longer C–O distance than the ground state and is pyramidalized about the carbon atom (as are many substituted methyl radicals). In the case of silaketones we can make the following predictions. (a) Since the strong interaction of the silyl groups with the CO π* orbital (vide supra) will remove antibonding electron density from between the carbon and oxygen atoms in this orbital, we can expect the C–O distance in the excited state to be less than what it is in excited formaldehyde, cyclopropanone, or other alkylated ketones. (b) Maximization of the stabilizing negative-hyperconjugative interaction (Figure 2), or application of Bent's rules,[18] leads one to expect a smaller degree of pyramidalization about the carbon atom in silaketones than in formaldehyde, or alkylated ketone excited states. (Similar arguments can be used to explain

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[16] See, e.g.: Cotton, F. A. *Chemical Applications of Group Theory*, 2nd ed.; Wiley-Interscience: New York, 1971; p 186.

[17] See, e.g.: Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333.

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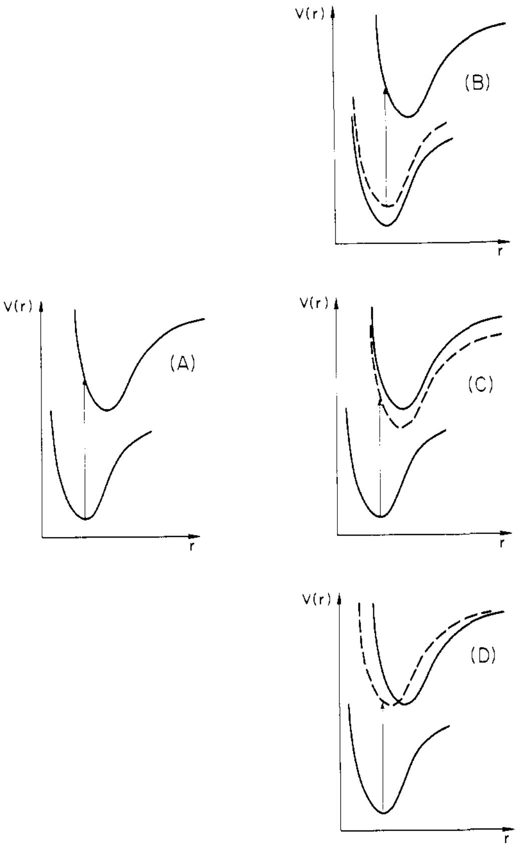

Figure 3. Three ways of lowering excitation energies. Part A represents an unperturbed system. In B, the ground-state energy has been raised (i.e., destabilized). In C, the excited state has been lowered (i.e., stabilized). In D, the minimum in the excited state is shifted to more closely coincide with the minimum in the ground-state potential energy surface.

the simultaneous increased planarity and decreased basicity of silyl-substituted amines.[19]) (c) In the case of disilacyclopropanone and disilacyclopropanimine, we can expect, since the newly occupied orbital is completely ring bonding, that the Si–Si distances will be shorter than in the ground state. We might expect the C–Si distances to be shorter as well for the same reason, but recall that RBBB found a significant mixing between the metal–carbon σ bonds and the nonbonding orbitals. It is not obvious which effect, removal of an electron from a partially σ-bonding orbital or placement in a π-bonding orbital, will dominate in the determination of the C–Si bond distance.

Considering points a and b above, we arrive at a third reason why acylsilanes are colored when alkyl ketones are colorless. To (1) RBBB's observation that metal–carbon bonds mix in with, and destabilize, the oxygen lone pair (see Figure 3B), and (2) BAS's finding that there exist lower lying vacant orbitals in silaketones (see Figure 3C), we must add (3) *that the excited-state geometries of the silaketones are more similar to their ground-state geometries than are those of the alkyl ketones.*[20] *In other words, in silaketones the vertical excitation energy is closer to the adiabatic excitation energy (see Figure 3D).*

This also provides a simple explanation for the more highly structured solution-phase UV-absorption profiles in the silaketones. First, the smaller C–O displacements in the acylsilane excited state lead to larger Franck–Condon factors and higher intensities, and, second, a more nearly planar excited-state geometry will lead to less activity in the low-frequency out-of-plane motion and less congested excitation profiles, thus better exhibiting the C–O stretching progression.

We must emphasize that, while we have primarily discussed silaketones, the results presented here apply just as well to the well-known[1-7] germa- and stanna-substituted ketones, metalloid-substituted imines, and other case I and case II chromophores as enumerated by West.[4] All of these molecules should have π-LUMO's of the same general form as that shown in Figure 1 for disilacyclopropanone. Open-chain molecules, of course, will not have the metal–metal bonding interaction present in the cyclic species, but their LUMO's will be of the same basic form; i.e., they will be bonding between the chromophore and the metalloid, and metalloid-substituent antibonding. Through withdrawal of electron density from the chromophore antibonding orbital, we can expect excited-state geometries to look more like ground-state geometries than in alkyl- or aromatic-substituted molecules, thus contributing to low excitation energies and colored compounds.

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(20) In addition to more planar excited states with shorter C–O bond distances, the silaketones, as evidenced by lower C–O stretching frequencies in the IR,[1,2] are expected to have *longer* C–O distances than alkyl ketones in their ground states.