

## ON THE ELECTRON AFFINITY OF PERFLUOROCYCLOALKANES AND PERFLUOROALKANES\*

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### SUMMARY

There is an increasing body of evidence showing that perfluorocycloalkanes have a higher electron affinity than their open chain analogs, the perfluoroalkanes. A new molecular orbital model is presented to explain these results and compared with the electrostatic model of Mittal and Libby. Explicit experiments are suggested which would allow comparison of the two models.

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### INTRODUCTION

There is an increasing body of evidence showing that perfluorocycloalkanes have a higher electron affinity than their open chain analogs, the perfluoroalkanes<sup>1-4</sup>. Thus Mittal and Libby<sup>1</sup> noted that  $\gamma$ -irradiation of gaseous alkanes yields hydrogen. This product arises from a recombination reaction of high-energy electrons with the alkane radical cation. Perfluorocycloalkanes decrease the yield of hydrogen,  $G(\text{H}_2)$ , by functioning as electron scavengers while the acyclic perfluoroalkanes have no effect. Naff *et al.*<sup>2</sup> reported that the logarithm of the lifetime of a fluorocarbon radical anion is proportional to the number of vibrational degrees of freedom it has, while Rajbenbach<sup>3</sup> from studies in solution showed that perfluoroalkanes again scavenge electrons more efficiently than perfluoroalkanes but that in this case *both* types of molecule quantitatively reduce  $G(\text{H}_2)$ . Finally, Hammond<sup>4</sup> has shown that perfluorocycloalkanes reversibly dissolve in the powerful electron-donating solvent tetrakis(dimethylamino)ethylene. Solution is accompanied by "stable spectral changes". In contrast, perfluoroalkanes do not form any charge-transfer complex and the solution is colorless.

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Though equivalent data exist ranking perfluoroarenes as more electron-seeking than the saturated perfluorocarbons, no discussion will be made owing to the great difference of the reactivity of those two classes of compounds to nucleophiles in general<sup>5,6</sup>. Mittal and Libby<sup>1</sup> argued that conventional molecular orbital logic is incapable of explaining the facile addition of an extra electron to saturated perfluorocarbons. More precisely, an extra electron would be expected to be in a strongly antibonding orbital if bonding considerations are limited to the "classical" s and p orbitals of C and F. They suggested "intramolecular electrostatic traps" arising from arrays of highly positively charged carbon atoms. In addition, Coulomb's law allows one to predict that a ring of positive charges will hold a negative charge better than a linear array. This explains the greater electron-scavenging ability of perfluorocycloalkanes. Hammond<sup>4</sup> attributed this ability either to the possibility of electrostatic traps or to available  $\sigma^*$  orbitals but does not concern himself with details. The current article purports to show both by analogy and by a more thorough analysis of the molecular orbitals of perfluorocarbons that Mittal and Libby's assumed lack of available orbitals is false.

#### DISCUSSION

Molecular fluorine, like the perfluorocarbons, is formally a closed-shell, saturated molecule. However, it has an electron affinity of 3.1 eV<sup>7,8</sup>. One therefore may not conclude that closed-shell molecules have only a small electron affinity. Both oxygen and fluorine are electronegative elements. Therefore, let us compare the molecular orbitals of the "unsaturated"  $>C=O$  and the "saturated"  $>CF_2$  fragments, treating both as 4-electron problems. (Note, we are *not* talking about carbon monoxide and difluorocarbene.) The carbonyl group has occupied  $\sigma$  and  $\pi$  orbitals. Adding another electron yields the radical anion, and the  $\pi^*$  orbital becomes half occupied (see Fig. 1). Consider the difluoromethylene group. There are four orbitals (see Fig. 2) corresponding to those of the carbonyl group, the first two of which are occupied. It is experimentally unknown whether the  $\pi^*$  or

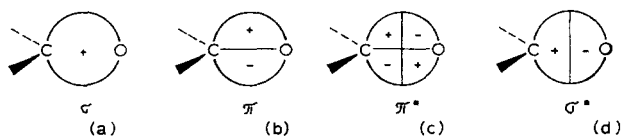


Fig. 1. Molecular orbitals of the 4-electron  $>C=O$  fragment.

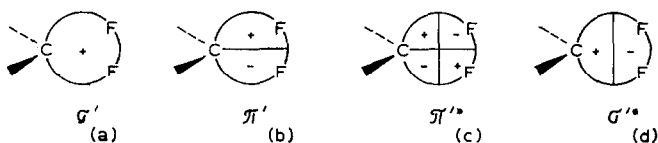


Fig. 2. Molecular orbitals of the 4-electron  $>CF_2$  fragment. It will be noted that the  $\sigma'$  orbital is the "sum" of the two normal C-F bonds, while the  $\pi'$  orbital is the "difference".

$\sigma^*$  orbital is lower in energy although the Author believes it is the latter because of the fewer nodes between the atoms. The Appendix gives two alternative heuristic arguments which reach the same conclusion. The high electron affinity of both F and  $F_2$  lowers the energy of the  $\sigma^*$  orbital relative to the corresponding one for  $>CH_2\cdot^-$ .

We may anticipate that the  $\sigma^*$  orbital remains vacant in polymeric difluoromethylenes, *i.e.* the perfluorocycloalkanes and perfluoroalkanes. As with the monomeric  $>CF_2$ , the addition of one more electron to  $-(CF_2)_n^-$  should yield partial occupancy of a  $\sigma^*$ -like orbital. So far, it made no difference whether  $-(CF_2)_n^-$  has "chemically imposed" periodic boundary conditions, *i.e.* ring formation, or is "capped" by two terminal fluorine atoms. We cannot add the extra electron to just one  $>CF_2$  group, but instead it must be added to the composite system of all the  $>CF_2$  groups. Thus we must consider some linear combination of  $\sigma^*$  orbitals. Let us contrast the highest occupied orbital of the radical anion of a hypothetical eclipsed  $-CF_2-CF_2^-$  unit and the nearly ubiquitous staggered conformer<sup>9</sup>. In both cases, there is C(2s)-C(2s) bonding. However, since this is common to both conformers, it will be neglected in later comparisons in this article. The eclipsed conformer has favorable overlap of all four fluorines whereas the staggered conformer has only pairwise overlap involving fluorines on the same carbon (see Fig. 3). (This ought *not* be compared with the interaction of two ethylenes to cyclobutane. Our problem involves a 2-center,1-electron + 2-center, 0-electron  $\rightarrow$  4-center,1-electron reaction, while the non-example is a 2-center,2-electron + 2-center,2-electron  $\rightarrow$  4-center,4-electron reaction.) This suggests that the eclipsed conformer should have the higher electron affinity. In addition, we may intuitively argue that the electron affinity monotonically decreases with increasing F-C-C-F dihedral angle and with increasing F-F distance.

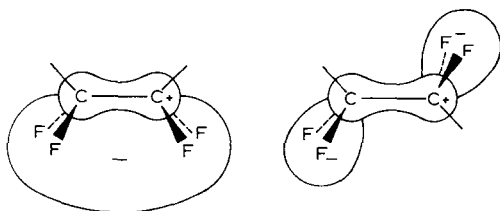


Fig. 3. Highest occupied molecular orbital in eclipsed and staggered  $-(CF_2)_2\cdot^-$ .

The above tacitly assumed that the geometry of the neutral  $-CF_2-CF_2^-$  is the same as that of the radical anion. This will continue to be assumed. Now consider the trimer  $(CF_2)_3$  chain\* and the cyclic tetramer  $(CF_2)_4$ \*\* , *i.e.* perfluoro-

\* In reality, the  $(CF_2)_3$  chain is probably twisted. Polytetrafluoroethylene, the "infinite" polymer of  $CF_2$ , has a helical backbone with a periodicity of 13  $CF_2$  units<sup>9</sup>.

\*\* We will assume that the perfluorinated cyclobutane is planar even though cyclobutane itself is known to be non-planar. This assumption is justified by the fact<sup>10</sup> that the inversion barrier in cyclobutane is only 1.3 kcal mole<sup>-1</sup>.

cyclobutane. For the  $(\text{CF}_2)_3$  chain, as with the staggered conformer of the  $(\text{CF}_2)_2$  chain, there is no "1,2" bonding. However, there is anticipated to be considerable "1,3" bonding (see Fig. 4). Using tetrahedral angles, a C-C bond length of 1.54

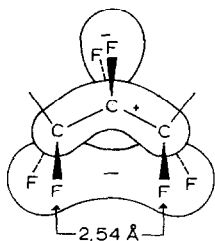


Fig. 4. "1,3" Bonding in the highest occupied molecular orbital in staggered  $-(\text{CF}_2)_3-\bullet^-$ .

Å and a C-F bond length of  $1.33 \text{ \AA}^{11}$ , elementary trigonometry gives the 1,2 F-F distance in  $-(\text{CF}_2)_2^-$  as  $2.37 \text{ \AA}$  and the 1,3 F-F distance in  $-(\text{CF}_2)_3^-$  as  $2.54 \text{ \AA}$ . By our assumption that electron affinity is inversely correlated to F-F separation, we predict the ordering for electron affinities:  $-(\text{CF}_2)_2^-$  (staggered)  $< (\text{CF}_2)_3 < (\text{CF}_2)_2$  (eclipsed). Since perfluorocyclobutane contains four staggered  $>\text{CF}_2$  groups while perfluorobutane contains four  $>\text{CF}_2$  groups as found in the  $(\text{CF}_2)_3$  chain, we correctly "predict" the former molecule should have the higher electron affinity. In addition, the cyclobutane has four "1,3" interactions at  $2.86 \text{ \AA}$  (see Fig. 5). It should be remembered at this time that for the neutral, normal fluorocarbons these non-bonded fluorine-fluorine interactions decrease the thermodynamic stability but increase chemical inertness by more uniformly "shielding" the highly positive carbon skeleton.

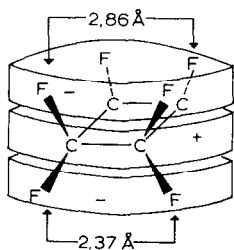


Fig. 5. "1,3" Bonding in the highest occupied molecular orbital in cyclic  $(\text{CF}_2)_4\bullet^-$ .

As with the cyclobutane, cycloalkanes have long-distance interactions. For example, consider the perfluorinated cyclohexane in the idealized chair conformation. It has each equatorial fluorine interacting with the four fluorines on the adjacent carbons. Two of these fluorines are equatorial and two axial. Each axial fluorine interacts with the two equatorial fluorines on the adjacent carbons and also has a "1,3" interaction with the remaining two fluorines on its own side of the molecule.

It is important to note that the models of Mittal and Libby and of the Author are inherently different. Most significantly, in the earlier figures of this article the + and - signs denoted the sign of the orbital, not the net charge on the atom. Orbital sign changes, and the associated nodal structure, directly relate to the kinetic energy, and, by the virial theorem\*, to the total molecular energy. Since Mittal and Libby's model is purely electrostatic, it may simply be said that the Author's model "refers to the kinetic energy, while Mittal and Libby's refers to the potential energy"<sup>12</sup>.

Two problems remain to be discussed. The first is the quantitative estimation of the electron affinities. In practice, this is almost impossible to accomplish. Straightforward calculation of the energy difference between a fluorocarbon and its radical anion is frustrated by the inadequacy of most calculational methods in studying anions. For example, even at the Hartree-Fock limit, the electron affinity of F is calculated to be only 1.4 eV, whereas the experimental value is 3.45 eV<sup>13</sup>. For comparisons among the various fluorocarbon radical anions, a much lower level of computational accuracy may be permissible\*\*†.

The second problem consists of choosing suitable compounds for testing the models. The Reader will note that one may not introduce a new chromophore (such as >C=O) into the molecule as it would serve as an automatic electron trap. A rather simple comparison is between (CF<sub>2</sub>)<sub>4</sub> and (CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>. By Mittal and Libby's logic, the Author would anticipate the relative electron-capturing ability would be in the ratio 4:3 corresponding to the ratio of the number of CF<sub>2</sub> groups. The latter compound is merely a slightly distorted perfluorocyclopropane, *i.e.* the three CF<sub>2</sub> groups are still in a ring. By the Author's model, the ratio would be closer to 2:1 corresponding to the number of "1,2" and "1,3" interactions. Clearly analogous comparisons may be made for other mono- or di-hydrogenated cyclic perfluorocarbons. Such a pair of molecules are the recently reported 1*H*-undecafluorobicyclo(2,2,1)heptane<sup>14</sup> and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane<sup>15</sup>. An intuitive application of Mittal and Libby's model suggests the ratio of electron affinities should be 11:10 corresponding to the number of fluorines. In contrast, the Author's model suggests closer to 1.8:1 as there are eight "1,2"

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\* The virial theorem allows one to say the negative of the kinetic energy is the total energy (I. N. LEVINE, *Quantum Chemistry*, Vol. 1, Allyn and Bacon, Boston, 1970, p. 429-442, and in particular p. 432).

\*\* Dr. A. Minton (unpublished results quoted in personal communication) used particle-in-the-box calculations to support Mittal and Libby's model when initially proposed. It should be noted that the particle-in-the-box approach in its simplest form relates only to the kinetic energy of the electrons and thus is conceptually closer to the Author's nodal symmetry logic than to Mittal and Libby's electrostatics description.

† In an *ab initio* quantum chemical study of the dissociation energy of OF<sup>-</sup>, the Author and Dr. L. C. Allen (unpublished results) have found that a minimal basis set is sufficient for comparing O + F<sup>-</sup> and O<sup>-</sup> + F. More precisely, the error in our computation for the electron affinity of O was almost identical to the error for F.

and six "1,3" interactions in the former but only four "1,2" and six "1,3" interactions in the latter. (See Figure 6. Also recall "1,2" interactions are more important than "1,3".)

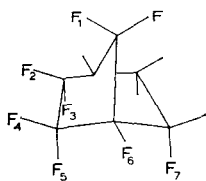


Fig. 6. Sample "1,2" and "1,3" interactions in highly fluorinated bicyclo(2,2,1)heptanes. "1,2": (2,4), (3,5), (4,5), (5,6). "1,3": (1,2), (5,7). All others may be found by symmetry.

If one leaves essentially perfluorinated hydrocarbons, other test compounds become reasonable. Mies<sup>16</sup> suggested the comparison of all-*cis*- and all-*trans*-1,2,3,4-tetrafluorocyclobutane. The former compound has four "1,2" interactions and two "1,3" interactions, while the latter has only two "1,3" interactions. Since "1,2" interactions are predicted to be more important than "1,3", we may predict that the all-*cis* compound should have an electron affinity at least three times that of the all-*trans*. Libby and Mittal's model would predict an identical electron affinity. The major complication of such a comparison is that the electron affinity of both isomers will be low and thus difficult to measure.

#### CONCLUSIONS

An alternative mechanism has been proposed to explain the higher electron-capturing ability of cyclic perfluorocarbons than of their linear analogs and several test compounds suggested.

#### ACKNOWLEDGMENTS

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#### APPENDIX: ALTERNATIVE HEURISTICS FOR THE CHOICE OF ORBITALS IN $>CF_2\bullet^-$

The first heuristic entails the isoelectronic comparison of  $>CF_2\bullet^-$  with  $>PF_2$  and  $>PCl_2$ . From EPR studies on  $PF_4$ <sup>17</sup> and  $PCl_4$ <sup>18</sup>, it is known that the extra electron is in the equatorial plane (*cf.*  $PCl_5$ ,  $SF_4$ ). It is thus in a  $\sigma$ -like orbital (as contrasted with a  $\pi$ ) for which the  $\sigma'^*$  orbital (Fig. 2(d)) is the related analog for the  $>CF_2\bullet^-$  system.

Alternatively, we may visualize  $>CF_2$  as having two strong bonds and one much weaker F-F bond. The orbital of lowest energy is both C-F and F-F bonding

(Fig. 7(a)). The next orbital may be either C–F bonding and F–F antibonding (Fig. 7(b)) or C–F antibonding and F–F bonding (Fig. 7(c)). Since the C–F bond in  $\text{CH}_3\text{F}$  is stronger than the F–F bond in  $\text{F}_2$ , we anticipate that the former combination is of lower energy. However, the latter is most definitely of lower energy than the orbital that is both C–F and F–F antibonding (Fig. 7(d)). As these orbitals (Fig. 7(a)–(d)) are equivalent to those in Figures 2(a), 2(b), 2(d) and 2(c) (note order) we may again conclude that the  $\sigma'^*$  orbital is probably occupied in  $>\text{CF}_2\bullet^-$ .

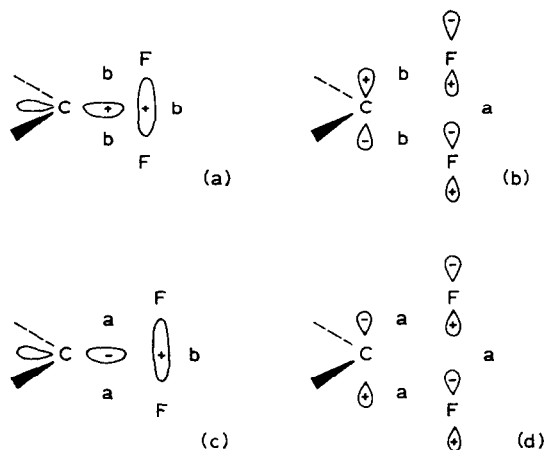


Fig. 7. Alternative bonding model for  $>\text{CF}_2\bullet^-$  (see Fig. 2); b means bonding, a means antibonding.

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