charges at carbon atoms adjacent to very electronegative atoms in the substituents (F, OR), the distributions of formal charge are very similar to those in **1** and **2a** (Tables X, XII).

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On a Recent Attempt to Apply Frontier Orbital Theory to Nucleophilic Aromatic Substitution

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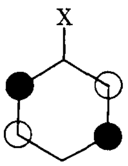
Abstract: The recent attempt by Epiotis and Cherry to apply frontier orbital formalism to nucleophilic aromatic substitution in polyhaloaromatics is criticized. It is shown that, contrary to the original claim, the method cannot be convincingly applied to substituted benzenes, and that it cannot give correct predictions in the cases of a number of perfluoropolycyclic aromatics for which experimental results are available. An extension of the older, "I_π-repulsion", method is presented which can rationalize the substitution reactions of these perfluoropolycyclics.

The recent publication[1] by Epiotis and Cherry of a frontier orbital (FO) method purporting to predict the orientation of nucleophilic substitution in polyfluorobenzenes and related species prompts us to reply. Their publication fails to give any convincingly coherent explanation of the experimental facts, and is, indeed, greatly inferior to one published[2] 10 years ago.

The essence of Epiotis and Cherry's FO approach is a consideration of the interaction between the LUMO of the benzenoid substrate and the HOMO of the incoming nucleophile. The latter orbital may be considered for practical purposes to be of at least cylindrical symmetry, and so attention focusses upon the LUMO of the substrate. Epiotis and Cherry analyze the problem of lifting the degeneracy of the two low-lying π-type benzenoid orbitals 1 and 2 in the presence of a substituent X and show that the FO hypothesis leads to the result that in C_6F_5X compounds where the substituent induced energy difference between 1 and 2 is large (i.e., X is a strong donor or strong acceptor of electrons), then either (1) substitution should be nearly all para to X (if 2 is lowest lying), or (2) equal amounts of substitution are expected meta and ortho to X (if 1 is). This latter prediction is obviously not in accord with experiment, and the authors seek to avoid the difficulty by invoking steric effects to disqualify ortho substitution.



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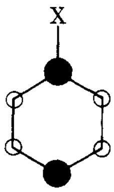

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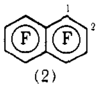
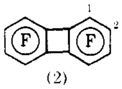
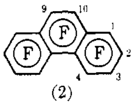
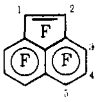
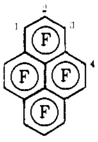
Even so, however, the FO approach does not explain the known facts: the experimental result is that, for clear-cut cases with strong acceptors (e.g., $C_6F_5NO_2$)[3] or donors (e.g., $C_6F_5NH_2$)[4] either (1) ortho and para substitution is observed with essentially no meta or (2) meta substitution is very predominant with little or no ortho or para product found. (There are, naturally, intermediate cases, but these are not germane here.)

The attempt to cover case (2), where experiment gives essentially all meta product, by saying that the simple FO method predicts ortho + meta attack, but ortho is ruled out by steric effects, is very difficult to sustain. Thus, reaction of pentafluorophenoxide ion with hydroxide ion gives essentially only meta product,[5] whereas the steric effect of O^- vs. F must be at best minimal, as indeed must that for NH_2 vs. F in pentafluoroaniline,[4] where meta substitution is again almost the exclusive reaction. It may thus be fairly concluded that the attempt to distort the FO conclusion to fit the experimental results fails here.

It should be pointed out here that these experimental observations are all satisfactorily rationalized on the older[2] "I_π-repulsion" theory, based upon electron repulsions in anionic Wheland intermediates, no universal steric effect being needed.

Turning now from benzenes to perfluoropolycyclics, where

Table I. Selected Hückel Coefficients,[14] Experimental Positions of Attack, and Values of θ (See Text) for Perfluoropolycyclic Aromatics

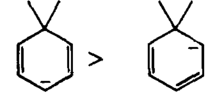
Substrate (position attacked by nucleophiles)		Hückel coefficients					θ (position)
 (2)		C_1	C_2				
	$\phi_6{}^a$	0.4253	0.2629				0.9091 (1)
	ϕ_7	0.0	0.4083				0.8750 (2)
	ϕ_8	0.3996	0.1735				
 (2)	$\phi_7{}^a$	0.1640	0.2955				0.4444 (1)
	ϕ_8	0.4220	0.2246				0.5883 (2)
	ϕ_9	0.3685	0.1640				
 (2)		C_1	C_2	C_3	C_4	C_9	0.8276 (1)
	$\phi_8{}^a$	0.3402	0.0421	0.3147	0.2325	0.4150	0.7619 (2)
	ϕ_9	0.2730	0.3886	0.0258	0.3687	0.1010	0.7917 (3)
	ϕ_{10}	0.2213	0.1438	0.3855	0.2967	0.1851	0.8077 (4)
							0.8387 (9)
 (3)		C_1	C_3	C_4	C_5		0.9500 (1)
	$\phi_7{}^a$	0.5140	0.2109	0.0519	0.2400		0.5202 (3)
	ϕ_8	0.2305	0.1202	0.3223	0.3879		0.7399 (4)
	ϕ_9	0.0	0.4083	0.4083	0.0		0.5965 (5)
 (1)		C_1	C_2	C_4			0.7143 (1)
	$\phi_8{}^a$	0.0	0.3685	0.2955			0.7777 (2)
	ϕ_9	0.4241	0.1865	0.1385			0.8823 (4)
	ϕ_{10}	0.0	0.0	0.4083			

[a] LUMO.

little work has been published on rationalizations of substitution patterns, and the general philosophy of the FO approach might be thought likely to prove fruitful, we have compared the results of experiment with the predictions made by using Epiotis and Cherry's FO method on the simple Hückel orbitals of the parent nonfluorinated aromatics. Here there is no degeneracy of orbitals, and thus no perturbation of orbitals by ligands need be considered.

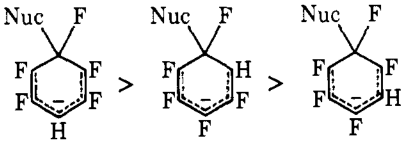
In fact, the method fails in three of the five cases for which experimental evidence is available (Table I); the only successes are with octafluorobiphenylene[6] and decafluoropyrene,[7] where 2 and 1 substitution, respectively, are correctly predicted. Perfluoronaphthalene[8] and phenanthrene[9] require that the LUMO and the next higher energy orbital be reversed in order for correct predictions to result; perhaps this might occur with orbitals derived from more sophisticated calculations,[10] but even if it does, Epiotis and Cherry's claim ("one can deduce the preferred orientations with a minimum of work and elaborate calculations") must be rejected for polycyclic compounds. There is a particularly severe difficulty in the case of octafluoroacenaphthylene, where experiments[11] using methoxide as nucleophile have demonstrated the order of substitution to be C_3, C_8, C_5, C_6, an impossible sequence in the FO formalism. Even prediction of C_3 requires that the LUMO should actually be ϕ_9 (see Table I), not ϕ_7, and then attack at C_4 is predicted to be *equivalent* to that at C_3.

While the major point of the present paper is the refutation of Epiotis and Cherry's theory, we also present, at a referee's request, a simple extension of the original[2] "I_π repulsion" theory which does account for the pattern of substitution in these perfluoropolycyclics. For simple, benzenoid, cases, the I_π thesis[2] is that nucleophilic attack on polyfluoro compounds would be fastest at the position which localized the least anionic charge on fluorine-bearing carbon atoms. In addition it was assumed, on the basis of other calculations, that the order of importance of canonicals was



> meta-localized form

and hence, for example, that the order of stability of the three possible intermediates from attack on pentafluorobenzene was



This accords with experiment,[12] where substitution mainly para to the hydrogen is observed, with some ortho and almost no meta.

A simple extension of this idea, applicable to the cases of polycyclic fluoroaromatics, is to sum the fractions of the anionic charge (HMO method, calculated[13,14] for the parent hydrocarbon) on fluorine-bearing carbons for each possible Wheland intermediate to give a parameter θ. Values of θ are given in Table I.

The position of substitution should be that which has the minimum value of θ. Octafluorobiphenylene is the only failure, and this can be corrected if conjugation across the cyclobutadiene system to the other benzene ring is ignored (that is, biphenylene is treated as a 1,2,3,4-tetrafluoro-di-X-benzene) —and this is not altogether unreasonable in this case. The major success is the prediction of the correct sequence for octafluoroacenaphthylene.

We claim no great theoretical depth for our treatment (or for the I_π repulsion theory generally) but it not only accords with current semiquantitative thinking in organic chemistry, but it works, which is more than can be said for the Epiotis and Cherry approach, and we therefore warn against the use of their misleadingly oversimplified variant of the FO method for the prediction of orientation in nucleophilic aromatic substitution.

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An Ab Initio Potential Surface for Phosphorane Fragmentation, $PR_5 \rightleftarrows PR_3 + R_2$

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Abstract: Calculations were performed to determine the favored mode of fragmentation for the $PH_5 \rightleftarrows PH_3 + H_2$ reaction using an 4-31G basis set. The addition of d orbitals to the basis set was found not to qualitatively affect the conclusions. The path of lowest energy for the reaction was found to involve a non-least-motion departure of an axial and an equatorial ligand. At the calculated transition state the axial bond was about 137% of its length in optimized PH_5 while the equatorial bond is actually slightly shorter (99% of its value in PH_5). Bonding interactions in the non-least-motion transition state are discussed as well as the relationship of the present work to other reaction types including oxidative addition. Eight degrees of freedom were investigated in constructing the potential surface.

The fragmentation of phosphoranes, $PX_5 \rightleftarrows PX_3 + X_2$, is a well-known and long-studied reaction.[1] It is possible to conceive, a priori, of different unimolecular mechanistic pathways for the process.[2] Using the trigonal bipyramid as our reference geometry, the X_2 atoms might, for instance, both originate from the axial positions of the PX_5. Alternatively, both might originate from equatorial positions, and last, one from an equatorial and the other from an axial site. We should consider also the use of a square pyramid, frequently considered as a transition state (vide infra) for ligand scrambling, as our reference geometry.

A complicating factor is that polytopal rearrangement of phorphoranes occurs with low-energy barriers.[3-5] Several different scrambling processes have been considered in the literature.[6] The problem caused by these rearrangements is simply that they provide a low-energy pathway (much lower than the calculated energy barrier for the fragmentation) for the interconversion of axial and equatorial sites in PX_5. Consequently, we need be quite careful in stating what we mean by the different reaction pathways since our starting system is fluxional.

The reaction may, of course, be viewed as occurring either forwards or backwards. An alternative perspective on the problem is obtained by considering the reverse reaction: the addition reaction of PX_3 and X_2. Here we have the PX_3 molecule bearing its lone pair interacting with a simple covalent molecule possessing both a filled σ and vacant σ^* orbitals. The lone pair is consumed during the course of the reaction and two new σ bonds are produced.

There are many reactions available for comparison having similarities in structural changes and, perhaps, in electronic effects as well. For example, the insertion reactions of singlet carbenes into the C–H bonds of saturated hydrocarbons bears a formal similarity.[7-9] While the mechanism of this reaction has been debated, most studies indicate a concerted transition state[8-10] rather than an abstraction recombination.[11] A theoretical study[10] by Dobson, Hayes, and Hoffmann favored a non-least-motion pathway.

The phosphorane addition reaction is also analogous to the oxidative-addition reactions encountered in the chemistry of coordinatively unsaturated transition metal complexes,[12-19] eq 1.

$$L_4M + XY \rightleftarrows L_4M(X)(Y) \qquad (1)$$

There have, in fact, been several studies where XY has been the hydrogen molecule. Vaska[20-22] has studied H_2 addition to $IrCl(CO)((C_6H_5)_3P)_2$. The dissociation of niobium trihydride complexes, eq 2, has been discussed.[23,24]

$$NbH_3(C_5H_5) \rightleftarrows NbH(C_5H_5)_2 + H_2 \qquad (2)$$

Iron pentacarbonyl can function as a hydrogenation catalyst.[25] The mechanism probably involves oxidative addition of H_2 to $Fe(CO)_4$, eq 3.[26]

$$Fe(CO)_5 \underset{CO}{\overset{-CO}{\rightleftarrows}} Fe(CO)_4 \underset{-H_2}{\overset{H_2}{\rightleftarrows}} Fe(H)_2(CO)_4 \qquad (3)$$

We wish to report ab initio calculations of the potential surfaces for the model system $PH_5 \rightleftarrows PH_3 + H_2$. Many other investigations[2,27-30] have been performed using PH_5 as a model. For the most part, the modelling has been fairly successful in reproducing the important aspects of the experimentally observable phosphoranes.

We wish to note several other relevant studies that have been performed. Clementi[31] studied the complex formed between NH_3 and HCl. Ohkubo, Kanaeda, and Tsuchihasi[32] have examined the least-motion approach of RX to $Co(CN)_5{}^{3-}$. Lucchese and Schaefer[33] have studied the charge transfer complexes formed between NH_3 or $N(CH_3)_3$ and F_2, Cl_2, or ClF. Last, we have studied the $PH_3 + H \rightleftarrows PH_4$ reaction.[34]