Tetrahedron Vol 28, pp. 3363 to 3367 Pergamon Press 1972. Printed in Great Britain

LONE PAIR INTERACTIONS IN FLUOROETHYL ANIONS

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(*Received in the USA* 8 *February* 1972; *Received in the UK for publication* 24 *March* 1972)

Abstract Calculations are performed on fluoroethyl and ethyl anions in the syn, anti, and perpendicular conformations with a range of semi-empirical molecular orbital methods containing varying amounts of directional character in the electron integrals. The nature of the interactions of the lone pair with the rest of the molecule is discussed.

IT WOULD be desirable to relate the various concepts or "effects" of organic chemistry as much as possible with exact theory. However, these can often be understood as being due to a limited component of the exact theory, better reproduced by more approximate methods, such as, for example, the HOMO-LUMO concept in Woodward-Hoffmann theory, *sigma-rho* relations, or any of a number of the empirical constructs of physical organic chemistry.

Semi-empirical MO theories are structured in terms of parameters, such as orbital electronegativity, which usually can be related to concepts in use in chemistry. The factorization and implicit approximations involved in these parameters provide a potentially fruitful area for the understanding of the nature of the interactions arising in organic chemistry. We have undertaken a program of investigating the "chemical" consequences of the parametrization of semi-empirical theories. A reasonable approach appears to be to perform a number of calculations on standard chemical systems with slightly varied methods and to note the response to the variation.[1-3] One has, in principle, the option of introducing a chemical "effect" through the inclusion or exclusion of terms within the treatment which can be considered to be due to the effect. Thus, for example, if a behavior pattern is believed to be related to some component of the MO theory, this component could be emphasized or de-emphasized within the theory to determine the effect on the predicted behavior. The extent to which the predicted behavior is sensitive to the variation would be a measure of the magnitude of the effect in the experimental situation. If several competing types of interactions exist in a molecule it may be possible to turn on and off those which are of interest, and thus to investigate the nature of results from single or combined effects.

One effect we are specifically interested in is that of lone pair-lone pair interactions. Here the possibility exists of including repulsion integrals with or without directional character. Consequently, it should be possible to dissect any effects which arise from the directional character of the lone pairs. One example of this has been reported for the case of the conformers of hexahydropyrimidine. It was shown that directional electrostatic effects are important and the concept of a directed lone pair appears to be valid.[3]

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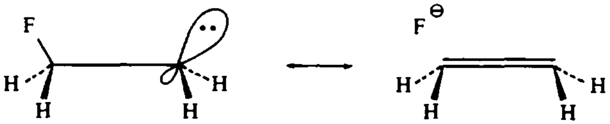
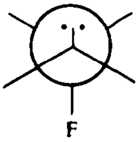
An investigation of the nature of fluorine hyperconjugation was previously reported by one of us, in which it was concluded that the effect of this anionic hyperconjugation in fluoroethyl anions was small.[4,5] However, because the method (CNDO/2) used in this approach uses repulsion integrals based on spherical potentials, it was not clear if the rotamers of fluoroethyl anion were strongly affected by the directional nature of the lone pair-fluorine interaction. We thus undertook a study where various sets of directional integrals were used, using the same approach and method (IRDO) as used for the hexahydropyrimidine work.[4,6]

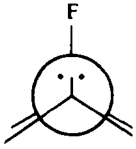


The IRDO (Intermediate Retention of Differential Overlap) method is a zero differential overlap approach of the NDDO type.[7] However, NDDO terms (integrals that preserve the directional characteristics of the basic atomic orbitals) are used only between "bonded" atoms. Between "non-bonded" atoms spherical integrals of the CNDO type are used.[7] One center terms including exchange integrals, are directional, as in the INDO method.[8] This study makes use of the capability of our program to be varied with respect to which atoms are "bound" in the above sense.

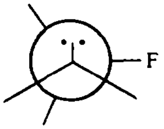
Calculations were performed using standard geometries. Tetrahedral angles were used. Bond lengths for C—C bonds were 1·54 Å, C—H bonds 1·09 Å, and C—F bonds 1·39 Å. Slater exponents of 1·2 for H, 1·625 for C, and 2·6 for F were used. Orbital electronegativities used were: C_{2s}, −11·02, C_{2p}, −2·577, F_{2s}, −19·00, F_{2p}, −3·160, H, −7·176 e.v. These are values appropriate to a method with one center exchange.



anti



syn



perpendicular

Table 1 summarizes the results using several sets of directional components for three possible conformations of the anion and parent molecule. The CNDO calculations previously reported have no directional integrals.[4] The INDO calculations do not have two center directionality, but must be included as the proper reference point for the succeeding calculations. The IRDO calculations include directional terms between bonded atoms. In addition, calculations, IRDO(C—F), were performed which deleted these terms between the two carbon atoms. The NDDO calculations include directionality between all atoms.

The neutral molecules exhibit similar predicted behavior for energies and rotational barriers at the different levels of calculation. Charge distributions for the anions and the neutral molecules are also similar. On the other hand, the heterolytic dissociation energies to the anions are markedly different.

$$RH \rightarrow R^- + H^+$$

TABLE 1. ENERGIES OF CONFORMATIONS (e.v.)

Compound	Method	syn	perpendicular	anti
ethane	CNDO[a]	0·095	0·047	-511·689[b]
	INDO	0·094	0·046	-503·154[b]
	IRDO(C--F)	0·085	0·043	-515·089[b]
	IRDO	0·089	0·044	-517·603[b]
	NDDO	0·089	0·044	-517·578[b]
anion	CNDO[a]	27·381	27·349	27·317
	INDO	28·192	28·162	28·132
	IRDO(C—F)	31·551	31·524	31·498
	IRDO	31·947	31·926	31·906
	NDDO	31·922	31·882	31·842
F-ethane	CNDO[a]	0·087	0·043	-1241·618[b]
	INDO	0·080	0·040	-1204·114[b]
	IRDO(C--F)	0·071	0·035	-1220·178[b]
	IRDO	0·068	0·034	-1222·767[b]
	NDDO	0·066	0·040	-1222·713[b]
anion	CNDO[a]	26·587	26·689	26·579
	INDO	26·912	27·159	26·805
	IRDO(C--F)	30·264	30·705	30·202
	IRDO	30·528	31·543	30·765
	NDDO	30·617	31·126	30·211

[a] CNDO results are taken from ref. 4.

[b] The anti conformer of the neutral molecule is taken as the zero of energy for each molecule and its anion. The energy is reported as the total valence energy for the neutral anti species and as a difference for the other structures related to them.

Putting directional character into the repulsive interactions does make it relatively more difficult to produce the anion, because in effect it is more difficult to delocalize the anionic charge since it is now acting as a directed lone pair.[6] The IRDO approach yields a large barrier to rotation in the fluoroethyl anion but not in the ethyl anion. This is summarized in Table 2.

The contributions of the additional one-center terms in INDO appear to be relatively equal for all three conformers. The predominant effect of directionality seems to be not to increase the stability of the syn and anti forms of the fluoroethyl

TABLE 2. STABILIZATION OF FLUORINE ANIONS WITH RESPECT TO ETHYL ANIONS[a]

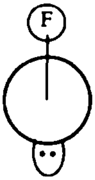
	syn	Perpendicular	anti
CNDO[b]	0·794	0·660	0·738
INDO	1·280	1·003	1·327
IRDO(C—F)	1·296	0·819	1·288
IRDO	1·419	0·383	1·141
NDDO	1·305	0·756	1·631

[a] The numbers represent a double difference between the amount of energy needed to produce a fluoroethyl anion compared to the amount needed to produce an ethyl anion. (e.v.)

[b] From ref. 4.

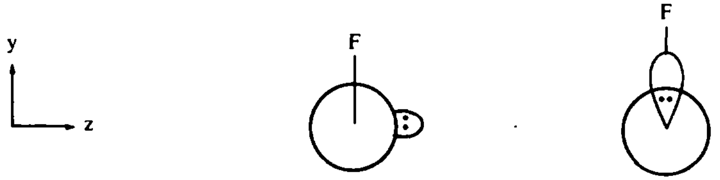
anion with respect to the ethyl anion, but rather to destabilize the perpendicular rotamer. That the source of this destabilizing interaction resides primarily in the C—C bond can be seen by comparison of the IRDO and the IRDO(C—F) results. The IRDO(C—F) results are quite similar to the INDO results but the complete IRDO increases the relative energy of (destabilizes) the perpendicular anion drastically.

The NDDO results indicate that in addition the long range electrostatic non-bonded CF interactions do exist as a major component stabilizing the anti-conformation with respect to the syn. The perpendicular form is intermediate. If the lone-pair were not directed this component would be relatively minor.



The nature of the C—C interaction which causes destabilization of the perpendicular conformer is of interest. This interaction must be due to the indirect action of the fluorine as it is not observed in the ethyl anion. An examination of the charges of the orbitals of the fluorine and the carbon bound to it is revealing (Table 3).

Table 3. Charges of orbitals on atoms in C—F bond



	Fluorine			Carbon		
	syn fluoroethane	syn anion	perp anion	syn fluoroethane	syn anion	perp anion
s	1·866	1·880	1·869	1·076	1·059	1·065
p-x	1·933	1·948	1·939	1·018	1·077	1·080
p-y	1·509	1·609	1·550	0·787	0·773	0·737
p-z	1·985	1·982	1·985	1·052	0·984	0·964

Fluorine appears to withdraw electrons in a sigma manner and donate in a pi-manner to the carbon of the C—F bond, resulting in a relatively electron rich pi component, p_z and electron poor sigma component, p_y. This realignment of electrons is evident in the neutral molecule, but does not make itself felt until it interacts with the lone pair. In fact, the electron distribution of the atoms of the C—F bond is only weakly dependent on the environment of the bond. The more occupied orbital is the perpendicular component and the repulsion of this more occupied orbital is higher in the perpendicular conformer as the lone pair is parallel to it. Consequently, there exists a destabilization.

We conclude that there still does not appear to be evidence for substantial stabilization by the mechanism of anionic hyperconjugation. Since the rotational preferences due to the interactions of the directional lone pair are factored out in the CNDO method we believe that such a spherical orbital method may in fact be the method of choice for ascertaining the presence of the effect that can be called fluorine hyperconjugation.

The above analysis shows the feasibility of using finite variations within a MO method to aid in the dissection of "effects" in organic chemistry. The particular methods do have their limitations, especially with regard to the effect of the zero differential overlap approximation.[2] However, the nature of the analysis is such that only a perturbation within the MO method is being investigated and thus the results should have more significance. If one attempts to analyze terms within a single MO method, the problem can be more complex because of the uncertainty as to how to partition energy terms.[9,10] We feel that approaches similar to that used here for other parameters may lead to other insights into chemical structure.

Acknowledgements—Grateful acknowledgement is made to the State University of New York at Stony Brook Computer Center for the computer time necessary for these calculations and to the Petroleum Research Fund for partial support of the project.

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