A Theoretical Molecular Orbital Study of the Allyl Ion Pair

**Fernando Bernardi,*[1a] Nicolaos D. Epiotis,*[1b] and Ronald L. Yates[1b]**

Contribution from Laboratorio C.N.R. dei Composti del Carbonio–Istituto di Chimica Organica dell'Università di Bologna, Bologna, Italy, and the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received August 12, 1974

Abstract: The allyl ion pair is discussed in terms of several important bonding concepts. Both semiempirical and *ab initio* SCF–MO calculations show that the stability of the ion pair is related to the degree of covalent bonding between the two formal counterions. Hydrogen bonding and acid catalytic effects are discussed in the light of current ideas concerning the role of intermolecular charge transfer in determining the bonding characteristics of molecules.

In recent years, there have been several important developments in the field of carbonium ion chemistry. The direct observation of carbonium ions in superacids,[2a] the precise definition of the concept of anchimeric assistance,[2b] and the discovery that ion pairs can play an important role in solvolytic reactions[3] are examples of such significant developments. This activity has stimulated considerable theoretical work which has primarily dealt with the structure of free carbonium ions.[4] On the other hand, the structure of ion pairs appears to have received little attention from quantum chemists. With this in mind, we undertook a qualitative SCF–MO study of the allylic ion pair which has been implicated in the rearrangement of allyl halides.[5] The choice of the model system has been dictated by the very fact that the allylic ion pair can serve as the prototype for the discussion of several important bonding concepts: (1) the subjacent orbital control of pericyclic bonding;[6] (2) the effect of back bonding on the stability of complexes;[7] (3) the effect of intermolecular charge transfer in determining bonding characteristics of molecules or molecular complexes.[8]

In this work, semiempirical INDO[9] calculations as well as nonempirical *ab initio* calculations of the various geometries of the allylic ion pair are reported. Emphasis is placed not on the absolute magnitudes of the calculated quantities but rather on the qualitative trend. Allyl fluoride and allyl chloride have been chosen as the model substrates. Since the qualitative conclusions regarding the corresponding ion pairs are identical, we shall only discuss the ion pair of the allyl cation and the fluoride anion.

The first task that we undertook was to determine the relative energies of the unsymmetrical and symmetrical ion pairs. In both semiempirical and *ab initio* calculations F was allowed to move from C_1 to C_3 of the allyl group at a distance of 1.80 Å above the plane of the allyl framework and along the hypothetical line connecting C_1 and C_3.
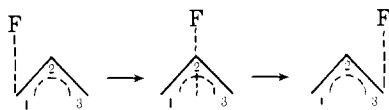
The *ab initio* computations have been carried out at the STO-4G[10] level of sophistication by using the Gaussian 70 series of programs.[11] We have first fully optimized the geometry of the allyl cation,[12] which has subsequently been kept constant (at the computed values) in the computation of the energy variation which accompanies the migration of F from C_1 to C_3.

In the INDO computations the geometry of the allyl framework was computed by reference to standard bond lengths and bond angles.[9]

The comparison between *ab initio* and INDO results can be seen in Figure 1. In both cases there is a barrier to the allylic rearrangement and the symmetrical form represents the transition state for the rearrangement.[13] It is noteworthy that the semiempirical and *ab initio* approaches provide results which agree very closely and are also in good qualitative agreement with experimental findings of Sneen and his coworkers.[3] The π charges and gross charges of the two forms at the semiempirical and *ab initio* levels are shown in Charts I and II.
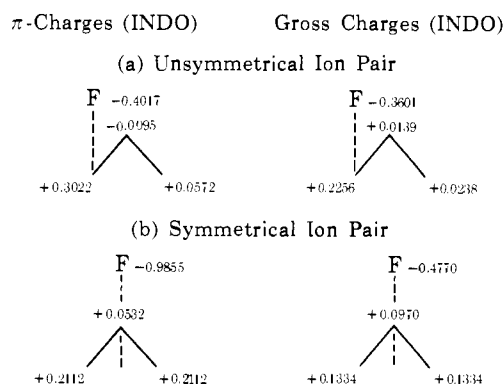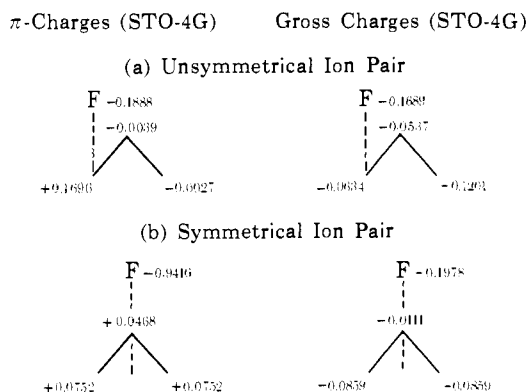
Chart I

π-Charges (INDO) Gross Charges (INDO)

(a) Unsymmetrical Ion Pair

(b) Symmetrical Ion Pair

Chart II

π-Charges (STO-4G) Gross Charges (STO-4G)

(a) Unsymmetrical Ion Pair

(b) Symmetrical Ion Pair

The term π charge is defined as the quantity $1 - n_\pi$, where n_π is the electron density of a p_z AO. The term gross charge is defined as $Z - n$ (STO-4G) or $Q - n$ (INDO), where Z is the atomic number, Q is the number of valence electrons of an atom, and n is the gross electron density of an atom.

From the comparison of the data listed in the previous chart, it can be seen that, while the values of the π charges computed at the INDO and *ab initio* levels are in good qualitative agreement, the agreement is much less satisfactory in the case of the gross charges. However, in this case the differences are caused mainly by the different polarization of the C–H bonds in the INDO and *ab initio* computa-
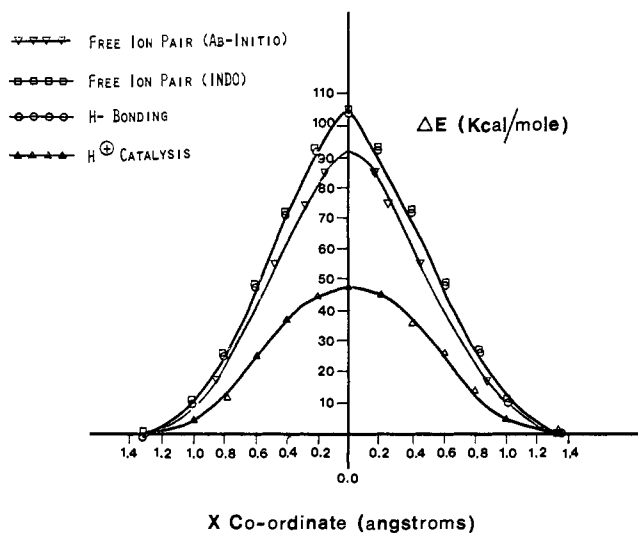
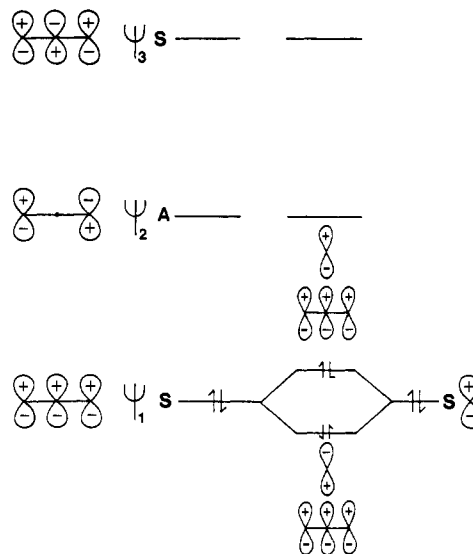Figure 1. Energy variation of the migration of F from C_1 to C_3.

Figure 2. MO interaction diagram for a polar [1,3] sigmatropic shift. The symmetric form represents the transition state of the rearrangement.
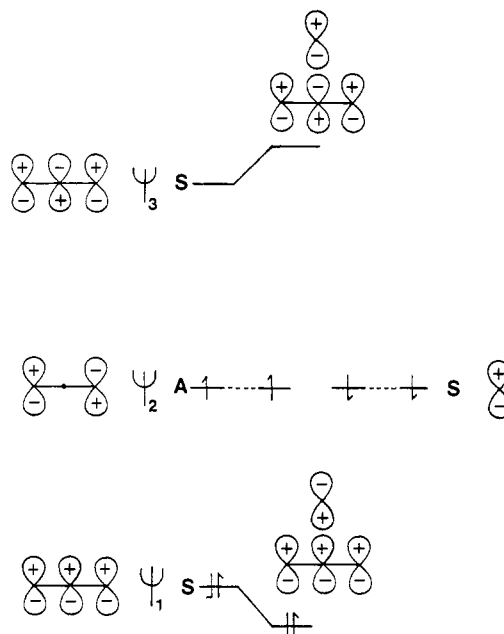

Figure 3. MO interaction diagram for a nonpolar [1,3] sigmatropic shift. The symmetric form represents the transition state of the rearrangement.

tions. In INDO computations, in fact, the gross charge at the hydrogen atoms of the C–H bonds is slightly negative, while in *ab initio* computations is positive. However, the same kind of qualitative trends are revealed by the two sets of data (INDO and *ab initio*). It is clear, in fact, that the degree of charge separation depends on the geometry of the ion pair, being maximal in the symmetrical form and minimal in the unsymmetrical form. In other words, the unsymmetrical form is a pseudo ion pair to the extent that there is very substantial covalent bonding between the two formal counterions. On the other hand, the symmetrical form is a true ion pair made up essentially of the allyl cation and the fluoride anion. As we shall see below, the degree of charge separation within the allylic ion pair, or the degree of covalent bonding between the two counterions, is an index of the relative stabilities of the various geometries of the ion pair.

We shall now examine the orbital interactions which are responsible for the relative instability of the symmetrical form. The principal orbital interactions involve the three allylic π MO's and the F_{p_z} AO. The dominant orbital interaction as illustrated in Figure 2 is between ψ_1 of the allylic MO's and the F_{p_z} AO and results in zero net bonding between the allylic fragment and F. This is an important result because it indicates that subjacent orbital control is *not important in stabilizing the transition states of allylic rearrangements in which the migrating group has a high ionization potential, i.e.,* subjacent orbital control does not occur in *polar* [1,3] sigmatropic shifts. Subjacent orbital control, however, is important in stabilizing the transition state of nonpolar [1,3] sigmatropic shifts. This difference between the polar and the nonpolar cases at the level of a one-configuration analysis can be seen in Figures 2 and 3. The importance of subjacent orbital control in each case depends directly on the ability of the p_z to interact appreciably with *both* ψ_1 and ψ_3. This occurs in the nonpolar but not in the polar case. In accordance with this analysis, the overlap populations of the p_z orbital of F and the p_z orbitals of C_1 and C_3 of the allyl fragment are expected to be near zero; our calculations confirm these expected trends and the results are given in Table I.

There is an additional orbital interaction which can be responsible for weak bonding of the allyl fragment and the leaving group in the symmetrical form. This orbital interaction involves the p_x lone pair of the fluoride anion and ψ_2 of the allyl cation and it is sketched below.

The calculated overlap populations reflecting this interaction are positive and are displayed in Table I.
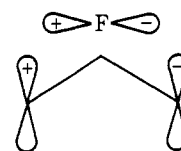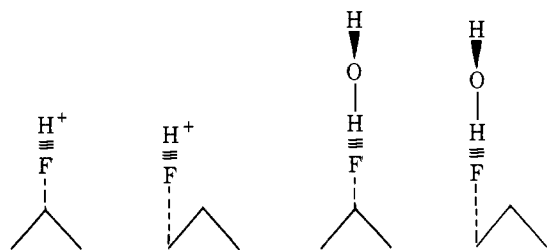
On the basis of these theoretical considerations, we are led to a rather simple picture of the allylic rearrangement. Specifically, covalent bonding of the ion pair is maximum in the unsymmetrical form as revealed by the overlap population data of Table I. In the course of the rearrangement, the degree of covalent bonding continuously decreases until the transition state, corresponding to the symmetrical form, is reached. It is apparent, then, that ion pairs are not devoid of covalent bonding. In fact, covalency determines the relative stability of various geometric configurations of a particular ion pair.

Table I. Bond Orders, Overlaps, and Overlap Populations (OP₁)ᵃ at the INDO Level and Overlap Populations (OP₂) at the *ab Initio* Level for Symmetrical and Unsymmetrical Allyl Fluoride Ion Pair
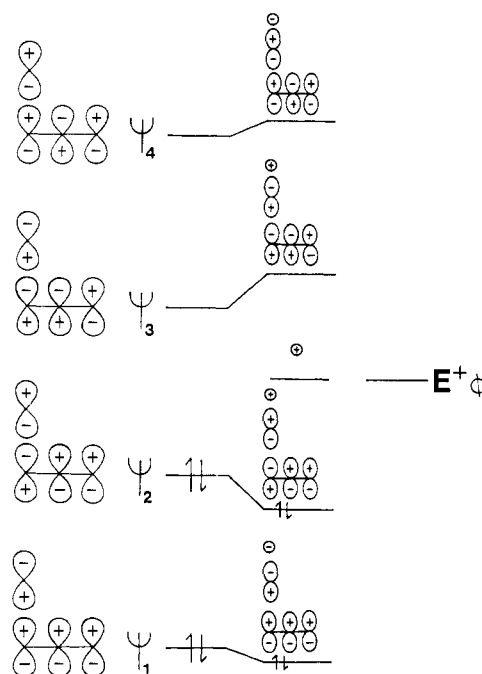
	C_{p_z}–F_{p_z}				C_{p_z}–F_{p_z}			
	Bond order	Overlap	OP₁	OP₂	Bond order	Overlap	OP₁	OP₂
				Symmetrical				
C₁–F	−0.0717	0.0437	−0.0031	−0.0699	0.6055	0.0423	0.0256	0.0208
C₂–F	−0.1100	0.0989	−0.0108	−0.0033	0.0000	0.0000	0.0000	0.0000
C₃–F	−0.0717	0.0437	−0.0031	−0.0699	0.6055	0.0423	0.0257	0.0208
				Unsymmetrical				
C₁–F	0.8283	0.1544	0.1279	0.1201	−0.0189	0.0000	0.0000	0.0000
C₂–F	0.0003	0.0299	0.0000	−0.0019	0.0475	0.0294	0.0014	0.0008
C₃–F	−0.3376	0.0023	−0.0008	−0.0012	−0.0440	0.0050	−0.0002	−0.0004

ᵃ OP₁ = Bond order × overlap.
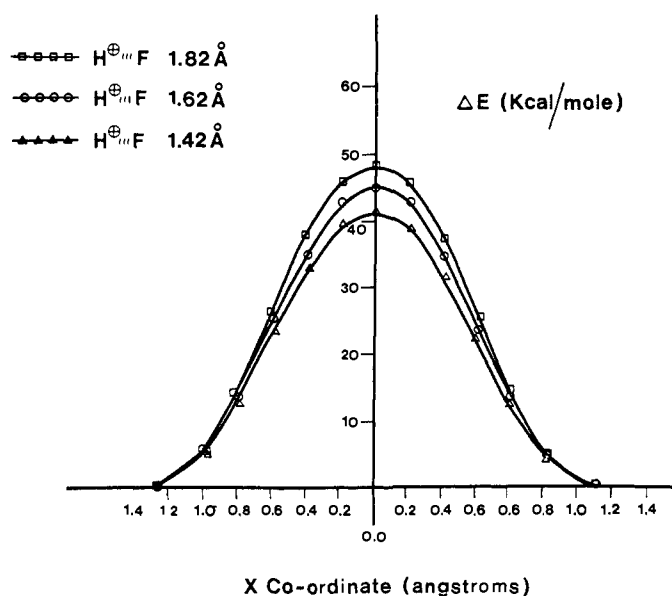
Figure 4. Dependence of the energy barrier to rearrangement on the coordination distance between F and H⁺.

Figure 5. MO interaction diagram for the interaction between an electrophile and the unsymmetrical ion pair.

Up to now, the model which we have described has been a gas phase one. In an actual solvolytic reaction, there are the additional effects of hydrogen bonding and acid catalysis which are to be considered in order to arrive at some reliable conclusions. We have examined the effect of coordination of H_2O and H⁺ with the allylic ion pair and this problem has been investigated only at the INDO level. The good agreement obtained in the previous computations of the energy variation at the INDO and *ab initio* levels provides confidence in the reliability of the INDO results in these two similar problems. The symmetrical and unsymmetrical coordinated allylic ion pairs are shown below. The

energy variation which accompanies the migration of F- - -H⁺ and F- - -H–O–H from C_1 to C_3 of the allylic fragment is shown in Figure 1. Hydrogen bonding has no effect. On the other hand, coordination of F by a proton dramatically reduces the barrier to migration by lowering the energy of the symmetrical form much more than that of the unsymmetrical form. This was found to be true for three typical cases regardless of the assumed distance between F and H⁺.

The dependence of the barrier height on this distance parameter is shown in Figure 4. It is clear that shorter F- - -H⁺ distances tend to produce a greater reduction on the height of the barrier.

The catalysis effect revealed by the calculations can be simply understood through some current concepts regarding the effect of charge transfer on the bonding properties of molecules. The interaction of an electrophile E⁺ with the symmetrical or unsymmetrical ion pair involves, principally, the HOMO of the ion pair and the vacant orbital of the electrophile. A consequence of this interaction is that charge transfer from the former to the latter orbital occurs. In the case of the unsymmetrical form, there is removal of bonding electron density between F and C_1 and development of bonding electron density between F and H⁺ (Figure 5). Since the two effects are energetically opposite, one expects no drastic influence of coordination on the energy of the unsymmetrical form. However, in the case of the symmetrical ion pair, there is removal of antibonding electron density between F and C_1 and C_3 and the development of bonding electron density between F and H⁺ (Figure 6). Both effects are energetically favorable and one expects a drastic lowering of the energy of the symmetrical form upon coordination. Calculations of the π bond order of the symmetrical ion pair confirm this prediction. The π bond order between an allylic carbon and the fluorine is taken to be

Table II. π-Bond Orders of the Symmetrical, Proton Coordinated, Ion Pair

	No coordi-nation π-bond order	1.42 π-bond order	F---H$^+$ distance, Å 1.62 π-bond order	1.82 π-bond order
C$_1$–F	−0.061	−0.022	−0.042	−0.044
C$_2$–F	0.047	0.038	0.014	0.019
C$_3$–F	−0.061	−0.022	−0.042	−0.044

Table III. Total Bond Orders and Overlaps of the Symmetrical, Proton Coordinated, Ion Pair[a]

	C$_{p_z}$-F$_{p_z}$ Bond order	Overlap
C$_1$–F	0.0441	0.0437
C$_2$–F	0.1650	0.0989
C$_3$–F	0.0441	0.0437
F–H	0.9061	0.1697

[a] F---H$^+$ distance is 1.42 Å.

equal to the sum of the p$_z$-p$_z$ bond orders of the two occupied π-type molecular orbitals. As can be seen in Figure 2, π_1 would represent a bonding interaction between C$_{p_z}$ and F$_{p_z}$ while π_2 an antibonding interaction. The π bond orders calculated by reference to these two MO's *only* are displayed in Table II. One can see that in the symmetrical ion pair coordination of a proton resulted in a change in the C$_{pz}$ − F$_{pz}$ bond order from *−0.061* to *−0.022; e.g.,* coordination of a proton reduced the magnitude to antibonding destabilization of the symmetrical ion pair. Furthermore, the dependence exhibited by the barrier to migration on the F--H$^+$ distance in Figure 3 can be easily correlated with the change in the π bond order as the distance between the fluorine and the proton is varied. As shown in Table II, the π bond order becomes more antibonding as the coordination distance increases. This results in destabilization of the symmetric ion pair as the F--H$^+$ distance becomes larger. Since the symmetric ion pair represents the energy maximum in the allylic rearrangement, destabilization of the ion pair results in an increase in the barrier to migration. Shorter F--H$^+$ distances, on the other hand, result in a lower barrier to migration due to a greater stabilization of the rearrangement transition state; *e.g.*, the C$_{p_z}$ − F$_{p_z}$ bond order becomes less antibonding. This is due to greater charge transfer from the HOMO of the ion pair to the vacant orbital of the electrophile since the magnitude of the charge transfer is directly proportional to the overlap of the interacting orbitals. Table III shows the total C$_{p_z}$ − F$_{p_z}$ bond orders calculated over *all* the occupied molecular orbitals of the ion pair complex. Coordination of a proton results in a change in the total C$_{1p_z}$ − F$_{p_z}$ bond order from *−0.0717* to *0.0441; e.g.*, the symmetrical ion pair becomes endowed with substantial covalent bonding.

Finally, the inability of hydrogen bonding to lower the barrier to migration can be traced to the high energy of the vacant σ^* orbital of H$_2$O. The energy separation of this orbital and the HOMO of the ion pair is apparently too large for any efficient interaction to occur and this precludes any substantial charge transfer.

The results of this study can be summarized by saying that the stability of an ion pair is directly related to the degree of covalent bonding present in the ion pair. Covalent bonding is indicated by positive and large bond orders between the two formal counterions. The perturbing environment can act upon the stability of the ion pair in a decisive
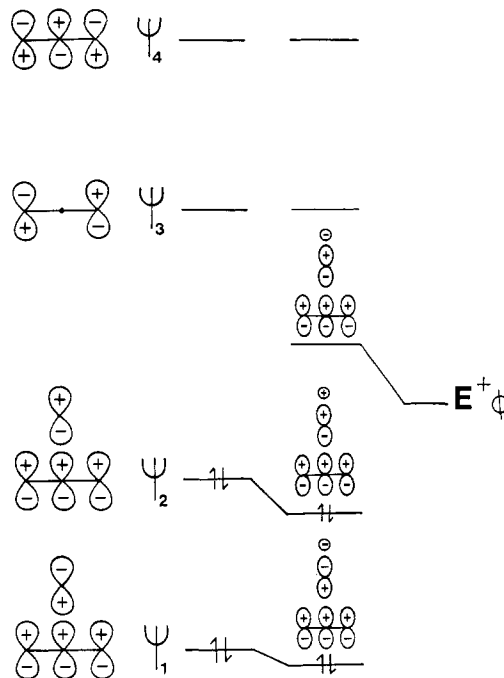
Figure 6. MO interaction diagram for the interaction between an electrophile and the symmetrical ion pair.

way by altering the covalent characteristics. Thus, solvent, hydrogen bonding, and catalysis can be used in a predictable manner to alter the kinetics of rearrangements which proceed *via* the intermediacy of ion pairs.

References and Notes

(1) (a) Laboratorio C.N.R. dei Composti del Carbonio; (b) University of Washington.
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(12) The geometry optimization of the allyl cation has been carried out at the STO-3G level.^{10} The computed values for the various geometrical parameters are: r(C$_1$–C$_2$) = 1.3831 Å; ∠C$_1$C$_2$C$_3$ = 120.19°; ∠HCH = 116.07°. The r(C–H) bond length has been kept constant at the value of 1.08 Å.
(13) The *ab initio* calculation for the symmetrical form did not converge satisfactorily. Then we have moved the F 0.03 Å away from the middle point and in this case we have been able to get a satisfactory convergence in the SCF procedure. Therefore the height of the barrier at the *ab initio* level comes from interpolation. Furthermore all the values of π and *gross charges* quoted in the text for the symmetrical ion pair *refer* to this situation. In particular the values for C$_1$ and C$_3$ are the result of an average of two slightly different values.