Organic Transition States. IV.[1] The Concerted Elimination of Hydrogen Chloride from Ethyl Chloride

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Abstract: We have used single determinant ab initio molecular orbital theory to study unimolecular elimination of hydrogen chloride from ethyl chloride. Three potential energy surfaces have been calculated. The first one corresponds to syn elimination, the second one to planar anti elimination, and the last one to nonplanar anti elimination. The reaction is predicted to be syn, and to occur via a planar four-membered transition state. A nonbonding pair of the chlorine takes a prominent part in the reaction mechanism, and is responsible for the allowedness of such a transition state (as first suggested by Goddard).

The pyrolysis of alkyl halides in the vapor phase has been extensively studied and is the subject of recent reviews.[3,4] Three mechanisms are possible for reactions in seasoned vessels: a radical chain mechanism; a radical nonchain mechanism; and a unimolecular mechanism E*i*, with the synchronous elimination of HX. In the particular case of chloro compounds, a general rule to determine whether or not the decomposition occurs by a radical chain mechanism has been stated by Barton and Onyon.[5]

"A chloro compound will decompose by a radical chain mechanism only so long as neither the compound itself nor the reaction products are inhibitors for the chain."

According to this view, ethyl chloride cannot decompose by a radical chain mechanism, as it gives the 1-chloroethyl radical $CH_3\dot{C}HCl$, which is an inhibitor, rather than the 2-chloroethyl radical $\dot{C}H_2CH_2Cl$, which could lose a chlorine atom and propagate the reaction. In the same way, 1,1-dichloroethane does not decompose by this radical mechanism,[6] while 1,2-dichloro alkanes do.[7-9]

The particular case of the dehydrohalogenation of ethyl chloride has been demonstrated by Barton and Howlett[6] to be an unambiguous example of unimolecular decomposition, with an activation energy rising to 60 kcal/mol. These authors confirmed their view in a later paper, using acetaldehyde for the detection of chain reactions.[10]

Many authors[11-16] tried to predict the aspect of the transition state. Maccoll and Thomas,[11] comparing the activation energy of a series of alkyl bromides with the corresponding homolytic and heterolytic CX bond dissociation energies, found a good correlation only in the latter case. They proposed a "quasi heterolytic" transition state, with an important polarization $C^{\delta+}\text{-}X^{\delta-}$, and a strong elongation of this bond. The departure of the halogen atom would receive assistance from the C–H bond. Later, Maccoll[12] proposed an ion pair model, modified by Benson and Bose,[13] who proposed a semi-ion pair model.

Methoxylation in α of ethyl chloride[14] strongly enhances the rate of the elimination while α-carboxylation[15] reduces it. These facts also support a highly polarized C–X bond in the transition state, while the weak effect of β substitution supports a moderately stretched C–H bond. However, a strong C–H elongation has been predicted, in the transition state, by Blades[16] on the basis of intramolecular primary isotope effects measurements, but this conclusion has been ruled out by Saunders and Cockerill,[4] who argued that, at the temperature of this experiment, a secondary isotope effect could be dominant.

Clear results are missing concerning the stereochemistry of the alkyl halides elimination reactions. According to the results of the pyrolysis of menthyl chloride[17] and neomenthyl chloride,[18] the unimolecular pyrolysis of alkyl chlorides seems to be a syn elimination occurring via a four-membered transition state. But the conclusions of the first experiment are not unambiguous, as pointed out by Harden and Maccoll.[19]

The aim of the present work has been to calculate a potential surface corresponding to the concerted unimolecular elimination of ethyl chloride and to determine the aspect of the transition state. Our results point strongly to a syn reaction, with a planar four-membered transition state. The conflict with the forbiddenness of 2s + 2s pericyclic reactions is only apparent. As we shall show, the chlorine atom destroys the pericyclic nature of the reaction (by bringing two atomic orbitals into play).

All calculations are ab initio and use the GAUSSIAN 70 series of programs.[20] The potential surfaces have been calculated at the STO-3G level of approximation,[21] while the 4-31G extended basis set[22] has been used to calculate the relative energies of the transition state and the alkane, leading to the activation energy of the reaction. The SCF wave functions are closed-shell single determinantal. As we will show below, a 3 × 3 configuration interaction, which might have been required to account properly for broken bonds, gives rise to very little stabilization for both reactant, products, and transition state.

Two potential surfaces have been calculated: the first one corresponds to syn elimination, where H and Cl stay on the same side of the C–C axis along the reaction; and the second one corresponds to a planar anti elimination, where H and Cl leave the reactant on both sides of the CC axis. In fact this last process does not occur, as we will show below.

Syn Elimination Potential Surface

Three reaction coordinates were chosen to describe the syn reaction: R, r_{HCl}, and r_{CC}. R is the distance between the middle of the HCl bond and the C–C axis; r_{HCl} and r_{CC} are the HCl and C–C bond lengths, respectively. The angles α, β_1, β_2 and the length δ, which were optimized on each point of the surface, are defined as follows (Figure 1): α is the angle between HCl and the C–C axis, β_1 and β_2 characterize the pyramidalization of the CH_2 groups, and δ describes the translation of HCl in a direction parallel to the C–C axis. The $H_1C_1H_2$ and $H_3C_2H_4$ angles, respectively θ_1 and θ_2, were kept equal to 112°, an intermediate value between 120° and 109°26′. These angles have been optimized, however, for the alkane and the transition state. The bond lengths $H_1\text{-}C_1$, $H_2\text{-}C_1$, $H_3\text{-}C_2$, and $H_4\text{-}C_2$ were fixed at 1.09 Å everywhere in the surface. Lastly, the ϕ_1 angle, expressing the twisting of the ethylene molecule, and the ϕ_2 angle, describing the rotation of HCl around the R axis, were kept equal to 0°. Nevertheless, optimizations of these angles have been carried out in various points of the sur-

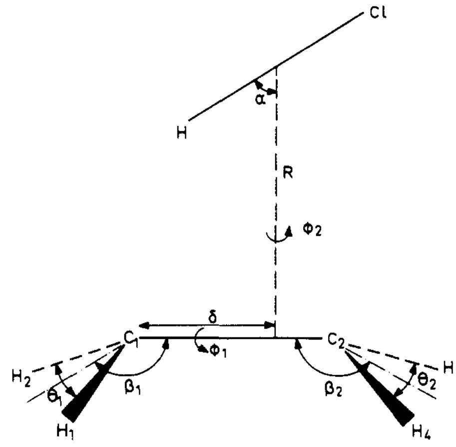

Figure 1. The coordinate system for syn elimination.

face, and the results always led to preserve the symmetry plane along the reaction.

At first a gross potential surface was calculated in order to determine approximately the main features of the transition state. The results were the following:

$$1.75\ \text{Å} < R < 1.9\ \text{Å}$$

$$1.48\ \text{Å} < r_{\text{HCl}} < 1.68\ \text{Å}$$

$$1.37\ \text{Å} < r_{\text{CC}} < 1.41\ \text{Å}$$

Then, within these limits, the calculation of a more detailed surface was carried out. This four-dimensional surface is not easy to visualize. For the sake of clarity, it has been reduced to three dimensions: R, r_{HCl}, and E, the potential energy (Figure 2). Fortunately, the full surface shows that, along the reaction path, r_{CC} is nearly a linear function of R. Thus these two parameters can be plotted on the same axis. In other words, for each value of R, the corresponding value of r_{CC} on the reaction path has been chosen to calculate E.

Transition State

From this surface we can deduce the coordinates R, r_{CC}, and r_{HCl} of the transition state. The results are the following: R = 1.859 Å, r_{CC} = 1.387 Å, HCl = 1.611 Å. The remaining parameters have been optimized, giving the following values: α = 46.9°, β_1 = 153.5°, β_2 = 1.75.7°, θ_1 = 116.4°, θ_2 = 115.8°, $\phi_1 = \phi_2$ = 0°. From these values one can deduce the C_1–H and C_2–Cl distances, which are 1.316 and 2.411 Å, respectively. The calculated energy of the transition state is −532.12431 hartrees at the STO-3G level, with a single determinant wave function, and −532.12503 hartrees with a 3 × 3 configuration interaction involving the two lowest excited states.[23] The reason for this poor stabilization lies in the different spatial localization of the highest occupied and lowest empty molecular orbitals. Indeed, it is well known that exchange integrals tend to be large only if the orbitals concerned overlap effectively.[24] It can be seen, in Figure 3, that the atomic orbitals composing the frontier molecular orbitals of the transition state have very different coefficients in the HOMO and in the LUMO orbitals. Consequently, the exchange integral between these molecular orbitals is weak, and the configuration interaction does not change drastically the wave function. Limited configuration interaction has also little effect on the energy of C_2H_5Cl, which is not surprising since this molecule is a closed shell saturated compound. On the contrary, 3 × 3 configuration interaction (CI) applied to the ethylene molecule stabilizes it by 25.9 kcal/mol, as the doubly excited state can interact strongly with the ground state. All together ethylene is well represented by a 3 × 3 CI, while the alkane and the transition state are best described with a multidimensional CI, where excitations are allowed to all the virtual orbitals. The situation is quite different for the second potential surface, where quasi diradicals are involved. In this case a configuration interaction, even limited, is absolutely necessary and gives very important energy improvements. Thus, in order to obtain comparable potential surfaces, we extended 3 × 3 configuration interaction to all calculations, in spite of its weak effect on the first surface.

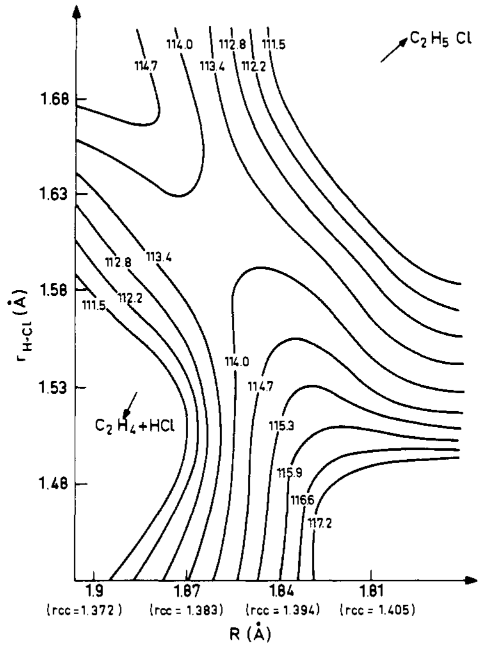

Figure 2. Potential surface for syn elimination. Energies are plotted in hartrees relative to the reactant, and calculated in STO-3G basis set.

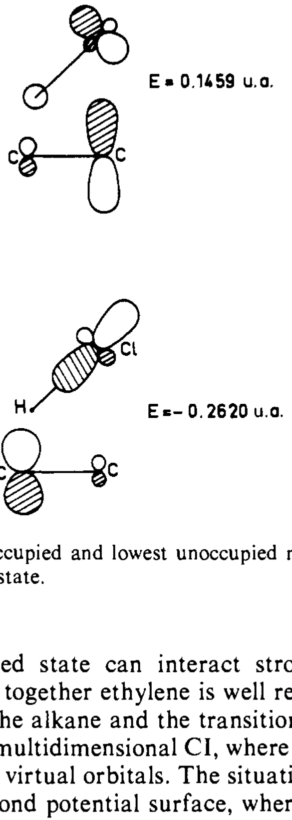

Figure 3. Highest occupied and lowest unoccupied molecular orbitals of the syn transition state.

The activation energy of the syn reaction has been calculated at the 4-31G level. The results are shown in Table I. To obtain the energies listed in this table we used the following geometries. For the ethylene molecule, the C–C bond length is 1.341 Å, and the HCC angle is 116.2°. These parameters have been optimized with the 3 × 3 CI, in STO-

Table I. Relative Energies of the Reactant, Products, and Transition State[a]

Basis set	C_2H_5Cl[b]	Transition state	C_2H_4 + HCl
STO-3G	0 (−532.30433)	113.0	59.8
STO-3G + CI	0 (−532.30474)	112.8	32.9
4-31G	0 (−537.51908)	69.6	21.3
4-31G + CI	0 (−537.51920)	69.2	6.7
Exptl[6]	0	60	15

[a] All energies are in kcal/mol. [b] In parentheses are reported the total energies (in hartrees) of the C_2H_5Cl wave functions.

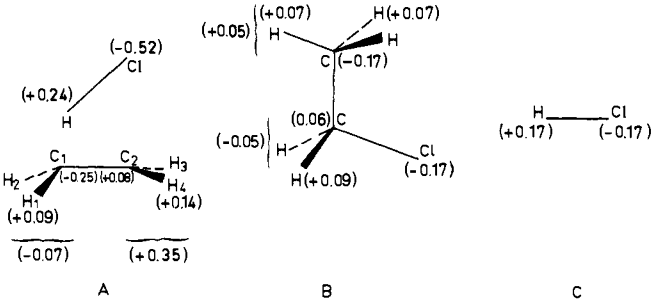

Figure 4. Charge distribution in the syn transition state (A), ethyl chloride (B), and hydrogen chloride (C), calculated in STO-3G basis set.

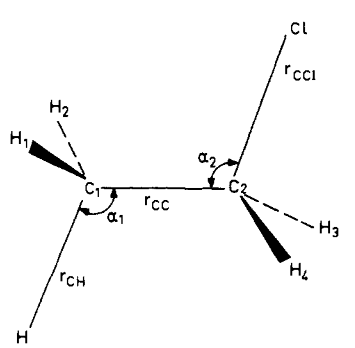

Figure 5. The coordinate system for planar anti elimination.

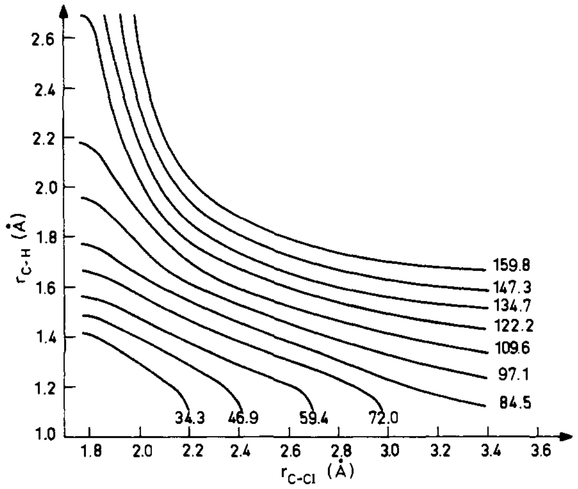

Figure 6. Potential surface for planar anti elimination. Energies are plotted in hartrees relative to the reactant, and calculated in STO-3G basis set.

3G basis set. All C–H bond lengths are 1.082 Å. For the alkane molecule, the C–C bond length is 1.54 Å, the C–Cl bond length is 1.77 Å, and all HCC angles are tetrahedral. Lastly, the HCl bond length is 1.28 Å. We obtained the value 69.6 kcal/mol without CI and 69.2 kcal/mol with a 3 × 3 CI. Both results are not too far from the experimental value (60 kcal/mol). In fact, the calculations using the 4-31G extended basis set are known to favor open structures with respect to rings.[25] For example, the calculated energy difference between a cyclobutene molecule and a transbutadiene molecule is higher than the experimental value by 8 kcal/mol.[26] This inconvenience does not occur with the more sophisticated 6-31G** basis set.[25]

Figure 4 shows the charge distribution in the transition state, compared with that in HCl and C_2H_5Cl. These charges have been calculated in STO-3G basis set, for this type of calculation gave a better dipole moment for HCl than the extended basis set. As predicted by experiment, there is an important charge transfer in the transition state, particularly onto Cl and C_2, if one takes into account that a carbon is electron attracting.

Anti Elimination Potential Surface

In order to make sure of the stereoselectivity of the reaction, another potential surface has been calculated corresponding to the planar anti elimination. Two reaction coordinates were chosen to describe this type of reaction: r_{CCl}, the C–Cl bond length, and r_{CH}, the C–H bond length (see Figure 5). The bond lengths C_1H_1, C_1H_2, C_2H_3, and C_2H_4 were kept equal to 1.09 Å. On each point of the surface, the atoms H, C_1, C_2, and Cl remained coplanar, the H_1C_1H and H_2C_1H angles were maintained equal to α_1, and the H_3C_2Cl and H_4C_2Cl angles were equal to α_2. The α_1 value was fixed to 109°26′ for CH = 1.09 Å, and varied progressively up to 90° along with the C–H stretching. Similarly, α_2 was associated with r_{CCl}; r_{CC} was also varied progressively along with both r_{CH} and r_{CCl}. To make a good guess at the α_1, α_2, and r_{CC} values, these parameters were optimized at one point, corresponding to r_{CH} = 1.35 Å and r_{CCl} = 2.3 Å. We found the following values: r_{CC} = 1.488 Å, α_1 = 104.6°, α_2 = 98.9°. The geometries of the other points of the surface were deduced by extrapolation. The surface, depicted in Figure 6, clearly shows that a concerted departure of the hydrogen and chlorine atoms needs a very high activation energy, as compared with the departure of a single atom, H or Cl. According to the potential surface, the Cl atom leaves the molecule more easily than does the H atom, but the corresponding activation energy, calculated at the 4-31G level, is 79.0 kcal/mol, which is higher, by 9.8 kcal/mol, than the syn transition state energy. This energy difference must be considered as a minimum since we have shown above that a ring is generally found too destabilized with respect to an open system, at the 4-31G level of approximation. Moreover, as pointed out in other papers of this series, some correlation energy is thus introduced in the diradical areas, and the energies in these areas tend to be slightly lowered relative to energies in "closed shell" areas. Lastly, such a single C–Cl cleavage would lead to a radical-type mechanism, which is ruled out by experiment. But it should be noted that this last potential surface corresponds to a planar anti reaction, where H and Cl do not interact. A third possibility remains: that of a transition state corresponding to a nonplanar anti reaction, with interaction between H and Cl, resembling the 2s + 2a addition of two ethylene molecules. We have calculated a rough three-dimensional potential surface for this type of reaction. In this calculation, representing the supra-antara approach of HCl to ethylene, H and Cl are taken on both sides of the ethyl-

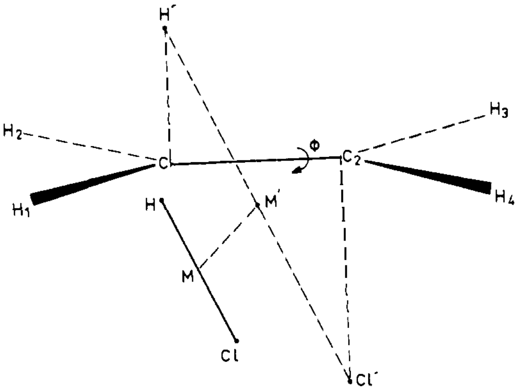

Figure 7. The coordinate system for nonplanar anti elimination.

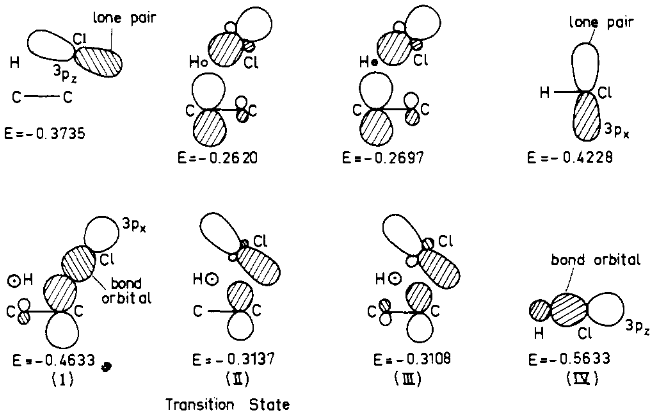

Figure 8. Some bonding molecular orbitals along the syn elimination. All energies are in hartrees.

ene plane, as shown in Figure 7. Along the reaction coordinate, the H-Cl axis was kept parallel to H′-Cl′, H′ and Cl′ being two dummy points above and below the ethylene plane. The other geometrical coordinates were $C_1H' = 1.09$ Å, $C_2Cl' = 1.77$ Å, angles $H'C_1C_2 = Cl'C_2C_1 = 90°$. If M′ is the H′-Cl′ midpoint and M the H-Cl midpoint, the axis MM′ is perpendicular to the C-C axis and parallel to the ethylene plane. The two variables along the reaction coordinate are MM′ and the H-Cl bond length. The C-C bond length and the ϕ angle, representing the twisting of the ethylene, are optimized at each point. This very rough surface gives a transition state with the following features: HCl = 2.1 Å, MM′ = 2.0 Å, $E = -537.27580$ hartrees, calculated in 4-31G basis set with 3 × 3 CI. The corresponding activation energy is 152.7 kcal. In spite of the roughness of the surface, this calculation seems to rule out a transition state of this type. So we can conclude that the unimolecular dehydrohalogenation of ethyl chloride cannot be an anti elimination. The elimination must be a syn reaction, occurring via the planar four-membered transition state deduced from the syn elimination potential surface, and described above.

Discussion

This thermic syn elimination could be considered as forbidden by Woodward-Hoffmann rules,[27] since it appears to be a 2s + 2s pericyclic reaction. Nevertheless, it is known[28] that these selection rules do not apply when an atom brings more than one orbital into play during the reaction process. In Figure 8 we show the behavior of the two 3p atomic orbitals of the chlorine atom contained in the symmetry plane of the reaction, say $3p_x$ and $3p_y$. In the alkane molecule (I), $3p_x$ is involved in a C-Cl bonding molecular orbital, while $3p_z$ carries a free electron pair. In transition state (II), $3p_x$ still interacts slightly with the carbon, and $3p_z$ still carries a free pair. In (III), representing a structure situated between the transition state and the final products of the elimination, $3p_z$ begins to interact favorably with the hydrogen, while $3p_x$ tends to carry a free electron pair. At last, in the HCl molecule (IV), $3p_z$ is involved in a HCl bonding molecular orbital, and a free electron pair is located in $3p_x$. So, it is clear that both $3p_x$ and $3p_z$ participate in the reaction. Consequently, the Woodward-Hoffmann rules cannot be applied to draw conclusions as to the forbiddenness of the reaction. In other words, the syn transition state involves a shift of six electrons rather than four, since a free electron pair of the chlorine participates in the reaction. This view is confirmed by a suggestion of Goddard[29] who showed, by application of the Orbital Phase Continuity Principle, that such a concerted dehydrohalogenation should occur if a nonbonding pair of the halogen takes a part. This is not without analogy with some results obtained by Mango and Schachtschneider,[30] who performed successfully the 2s + 2s cycloaddition of two ethylene molecules, by inserting, between the reactants, a nickel atom which brings two d atomic orbitals into play.

After the work was entirely completed, Tvaroška and coworkers[31] published an extended Hückel calculation in which they assume right at the outset that the process is syn. Their qualitative conclusions, as well as the general aspect of their syn transition state, are in good agreement with our results.

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Simulated ab Initio Molecular Orbital Technique. II. Benzenoid Aromatic Hydrocarbons[1a]

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Abstract: The successful application of the simulated ab initio molecular orbital (SAMO) technique to benzenoid ring systems is reported. Wave functions for benzene, naphthalene, anthracene, and phenanthrene were obtained through the transfer of Fock matrix elements from ab initio calculations on two "pattern molecules", *s-cis-* and *s-trans*-butadiene. The "pattern molecules" were calculated at geometries chosen to coincide with the benzenoid structure. The SAMO results for benzene are compared to a completely analogous ab initio calculation and the SAMO results for both benzene and naphthalene are compared to published ab initio results using other basis sets; the agreement is satisfactory and demonstrates that SAMO calculations can correctly predict features for the large molecules that are not present in the "pattern molecules". In all cases, the SAMO calculations were performed on computers of moderate size and used substantially less time and storage than is required for traditional ab initio methods.

Although ab initio calculations on a few large molecules of chemical interest are now beginning to appear in the literature, the prediction that such calculations would soon be routine[21] has yet to be realized. Such calculations are still terribly expensive and very demanding of computer resources; even for molecules of modest size, it is difficult to justify the cost of ab initio calculations if results of similar accuracy can be obtained much less expensively or with less elaborate computing facilities. The recently reported simulated ab initio molecular orbital (SAMO) technique[2] shows promise of providing just such an inexpensive means of calculating wave functions for large molecules using computers of modest size. The early results[2,3] indicate a rather successful mimicry of ab initio calculations using identical basis sets and geometries.

Earlier papers[2,3] reported the successful application of the SAMO techniques to saturated hydrocarbon chains and polymers. We demonstrate here the applicability of the SAMO approach to conjugated ring systems by reporting the results of SAMO calculations on benzene, naphthalene, anthracene, and phenanthrene. These systems provide a valuable test of the SAMO technique because: (1) they involve conjugated unsaturated systems; (2) rings are being simulated from "pattern molecules" which, in this case, are small open-chain molecules; (3) the geometry of these "pattern molecules" is chosen to mirror structural aspects of the molecule of interest; (4) we are able to simulate ab initio calculations on a whole range of large molecules by taking a limited number of these "pattern molecules"; and (5) we expect to be able to predict features in the large molecules that are not present in the "pattern molecules".

We would emphasize that our sole aim is to mimic ab initio results; hence our method, since it makes no direct appeal to the variational theorem, can only be judged by direct comparison with ab initio results or with experiment. Further, since the method avoids the calculation and storage of all two-electron integrals, it represents a considerable saving in both computer time and storage.

Method

The SAMO method arises from the observation by Eilers and Whitman[2] that matrix elements over the converged Hartree–Fock operator in an LCAO–SCF–MO treatment are closely similar for analogous pairs of basis functions in a range of similar molecules. Thus the converged Fock matrix elements from small "pattern molecules" provide an excellent estimate of the converged Fock matrix elements in large molecules; and hence they provide a direct noniterative means of calculating the molecular orbitals for large molecules. This transferability is neither readily seen nor easily exploited unless calculations are carried out in a basis of hybridized atomic orbitals. The reason for this is that hybrids point along bonds and are therefore defined by the internal reference framework of the molecule, while nonhybridized s and p functions are defined by reference to an often arbitrary external coordinate system.

Certain features of the SAMO methods circumvent many of the difficulties encountered by earlier workers on Fock matrix transference.[22,23] Since in SAMO both off-diagonal and diagonal elements are obtained by transference, there is no need to use the Wolfsburg–Helmholtz approximation[24] which is known to be unsatisfactory for kinetic energy. The use of hybrid orbitals with internally defined orientations permits a more precise identification of basis orbital types and environments while completely avoiding any need to explicitly consider rotational invariance. Moreover, the present availability and use of more and somewhat larger "pattern molecules" allows one to make more environmental distinctions and to demand greater similarity of "pattern" and "target molecules".

The SAMO Procedure. The SAMO method for closed-shell molecules generates the molecular orbitals and orbital energies by a single solution of the eigenvalue problem

$$\mathbf{FC} = \mathbf{SC}\lambda$$

where **S** is the matrix of overlap integrals (all of which are

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