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Extended Hückel Investigation of Reaction Mechanisms

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In 1962, in the course of a study of some boron hydrides, *Hoffmann* and *Lipscomb* (1) recognized that the nearest-neighbour assumption of Hückel theory was inapplicable for such molecules and proposed a reformulation of the Hückel formalism in which the zero-differential-overlap assumption was dropped. They pointed out that the validity of simple Hückel theory for aromatic molecules depends on the π -overlap between carbon atoms being small enough to meet the requirement that, if n is the number of atoms bound to a common atom, this overlap must not exceed $1/n$ (otherwise some S -matrix eigenvalues may become negative). Since this requirement was not fulfilled for the highly coordinated boron complexes, the complete S matrix was evaluated, and the full eigenvalue problem

$$(H - ES)C = 0$$

was considered, with a proportionality relationship between β_{rs} and S_{rs} . Other papers followed, in which the method was again used for polyhedral molecules (2), (3).

One year later, the new model took its final name of Extended Hückel Theory, and was cast in the concise, attractively simple form that has survived to date; in a comprehensive paper on hydrocarbons, *Ronald Hoffmann* (4) was able to show that many different properties of these compounds could be correctly calculated, thus establishing the operative validity of the method.

Using the valence orbitals as a basis set, the equations

$$(H - ES)C = 0$$

are solved, with the approximations:

$$H_{ii} = \alpha_i$$

$$H_{ij} = \frac{1}{2} K (H_{ii} + H_{jj}) S_{ij}$$

and subject to the orthogonality condition:

$$\delta_{ij} = \sum_{\mu, \nu} C_{i\mu} C_{j\nu} S_{\mu\nu}$$

The α_i are the valence ionization potentials of the corresponding basis orbitals. The constant K was given the value of 1.75. The overlap integrals were computed over Slater-type orbitals. The sum of orbital energies over the occupied orbitals was taken as the total molecular energy. Optimizations with respect to certain geometrical parameters could thus be carried out at reasonably low cost for many molecules, so that barriers to rotation and activation energies of rearrangements could be calculated; through Mulliken population analysis, overlap populations and charges were also obtainable.

Still, the reasons for this success were not quite clear; for instance, the good performance of the method in reproducing the equilibrium C-H bond distance in methane was thought to depend on fortuitous cancellation of the nuclear repulsion and of the change in

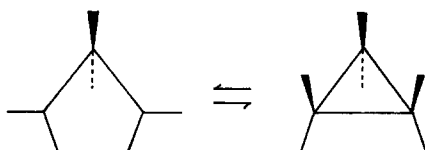
electronic repulsion from the atoms to the molecule. Moreover, excessive accumulation of charge on certain centres was found, especially in further applications to heteroatomic systems. The idea of an Iterative Extended Hückel Method emerged, in which the valence ionization potentials were related to the charge distributions in an iterative, self-consistent way. Dipole moments thus calculated for molecules containing oxygen and nitrogen are reasonable (5), but the limitations of the procedure soon became apparent, in that an inconsistency arises between ordinary Hückel-type variational formalism and the introduction of charge-dependent parameters (6).

Of the many discussions of the intrinsic properties of the Extended Hückel method, that of *Blyholder* and *Coulson* (7a) can be specially recommended. The validity of the above mentioned cancellation of repulsions seems to be substantiated (7b).

The incorrect estimation of charges and binding energies must therefore be accepted as an inherent feature of the method. This, in turn, implies that its main applications be of a qualitative rather than quantitative nature, leading to obvious limitations in the straightforward application of the theory to problems of chemical reactivity. Rewarding results can nevertheless be obtained by a judicious blend of calculation and chemical intuition; in this respect, one of the most powerful aids to the theoretical understanding of reactivity is the body of arguments that go under the denomination of orbital symmetry rules. The formulation and systematization of these rules came in a series of famous papers by *Woodward* and *Hoffmann* (8), whose arguments soon merged with the correlation diagram formalism of *Longuet-Higgins* and *Abrahamson* (9) into a now well accepted and far-reaching theory (10).

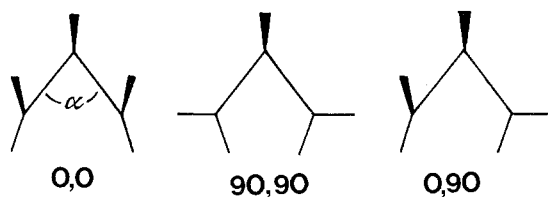
1. Trimethylene and Ring-Opening in Cyclopropane

A classical topic for illustration of the above principles is the analysis of the behaviour of the system: trimethylene \leftrightarrow cyclopropane \leftrightarrow methylene + ethylene (11). Ring closure of trimethylene is a simple example of an electrocyclic reaction (8a):



This process and the related questions of the electronic structure of substituted methylenes (12), (13) were the subject of careful analysis by Extended Hückel Theory (hence-

forth EHT) and orbital symmetry methods. When studying the opening of the cyclopropane ring, one finds that, considering the three possible geometries:



EHT energy minima are found for (0,0) in the conformation that most resembles closed cyclopropane (small α values), while the (0,90) and (90,90) conformations show local minima at $\alpha = 110^\circ$ ($E = 2.36$ eV relative to cyclopropane) and $\alpha = 120^\circ$ ($E = 1.93$ eV) respectively, in the ground configuration. For the excited configuration (in which the method cannot distinguish between singlet and triplet states) a somewhat flat energy surface is found. The first conclusion that can be drawn from inspection of this surface is that the double rotation of terminal methylenes in reactions involving opening of the cyclopropane ring should be favoured over single rotation by 0.43 eV.

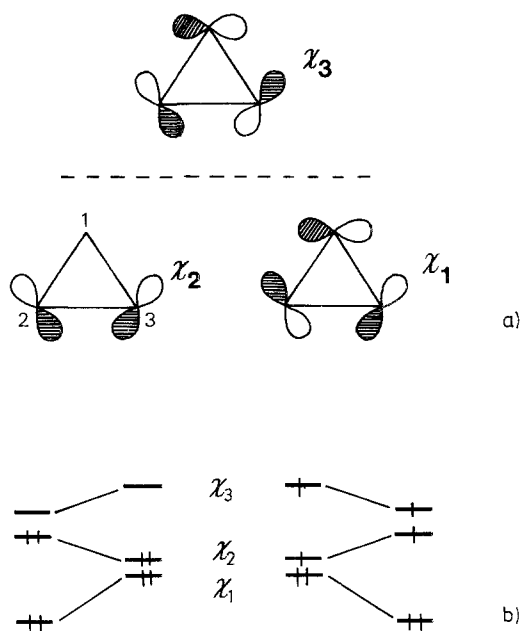


Fig. 1. a) The highest occupied and lowest unoccupied Walsh orbitals of cyclopropane. b) Ground configuration (left) and excited configuration (right) of cyclopropane, and level shifts upon increase of α .

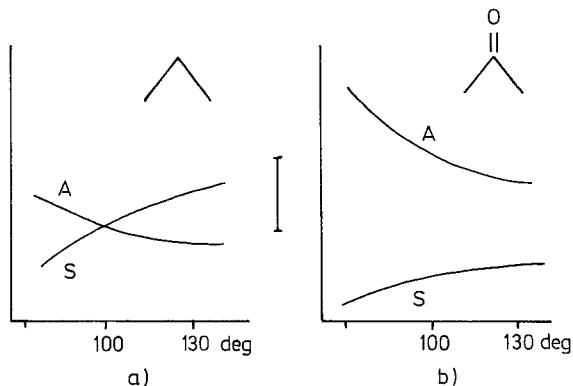


Fig. 2. a) Symmetric (*S*) and antisymmetric (*A*) levels of trimethylene: energy variation with increase of angle α (abscissa, degrees). b) The same for the oxyallyl radical. The vertical line is 1 eV on the energy ordinate scale.

The behaviour of the energy surfaces can be rationalized by detailed analysis of the shapes and energies of the relevant molecular orbitals. These are, as resulting from EHT wavefunctions, precisely the Walsh orbitals for cyclopropane (14) (Fig. 1 a). They can be labeled A and S (antisymmetric and symmetric) with respect to a mirror plane passing through the midpoint of the 2–3 bond. As this bond is stretched, the orbital χ_2 (2–3 bonding) is destabilized, and the orbitals χ_1 and χ_3 (2–3 antibonding) are stabilized. Two different fates are expected for the stretched ground configuration and excited configuration cyclopropane (Fig. 1 b). The 2–3 bonding character is partly preserved in the ground configuration, and a barrier to CH_2 rotation survives. Occupancy of the χ_3 orbital in the excited configuration, on the other hand, not only weakens the 2–3 bond, but the 1–2 and 1–3 bonds as well. Thus, a “floppy” excited configuration molecule is obtained, with no appreciable barrier to CH_2 rotation and much less stiff 1–2–3 angle bending.

Other properties of trimethylene emerge from an analysis of the shapes and symmetries of its relevant molecular orbitals. As the angle α becomes greater than 100° , the A and S levels cross (Fig. 2a). The explanation is that, as hyperconjugation destabilizes the symmetric orbital, the decrease of through-space 1–3 interaction stabilizes the antisymmetric orbital, thus making the corresponding energy levels cross (Fig. 3). Orbital symmetry rules require now that such a species should close to cyclopropane in a conrotatory manner (left):



The implications of these simple and clear-cut predictions, which have stimulated a great number of speculations and experiments, with an exciting feedback between theory and practice, will be discussed later.

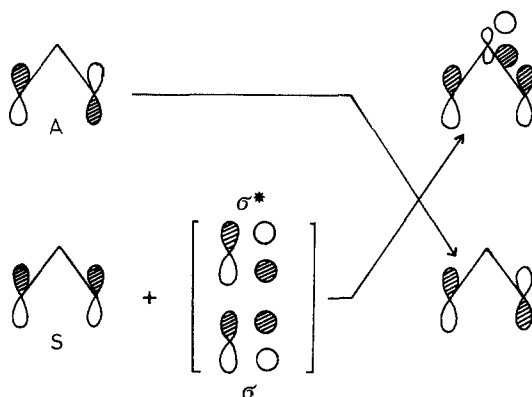


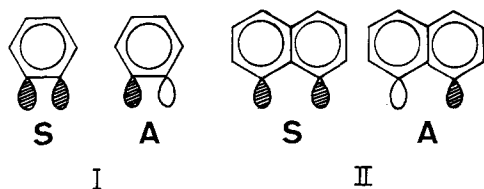
Fig. 3. Explanation of the level crossing in Fig. 2 a. α increases from left to right. The *A* level is stabilized by the decrease in through-space interaction; through-bond coupling (hyperconjugation) with the σ and σ^* levels of the interposed CH_2 destabilizes the *S* level.

The analogous calculations for the ring-opening of cyclopropanone to form the oxyallyl intermediate (*II*) give more pronounced minima in both the ground and excited configuration surfaces, and the *A* and *S* levels do not cross (see Fig. 2b). This requires, on orbital symmetry grounds, a disrotatory reclosure for oxyallyl.

A résumé of the properties and reactivities of small rings has been given by *Hoffmann* (15).

2. 1,2 vs. 1,4 Cycloadditions: Ethylene and Anti-Ethylene Structures

On orbital symmetry grounds, the addition of ethylene to ethylene with ring closure (cycloaddition) should be thermally forbidden. If one compares this reaction with the reaction of trimethylene with approaching ethylene and butadiene (Fig. 4), it is readily seen that, the *A* level being below the *S* level in trimethylene, the behaviour with respect to cycloaddition to olefins is reversed, that is, trimethylene is essentially an anti-ethylene structure. This principle can be generalized; for instance (16):



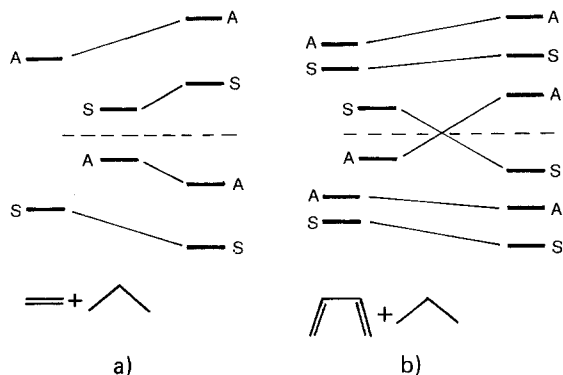


Fig. 4. a) Trimethylene + ethylene level diagram. b) The same for trimethylene + butadiene. *S* and *A* classification with respect to reflection in a plane bisecting angle α in trimethylene and passing through the midpoint of the double bond in ethylene and of the single bond in butadiene.

In *O*-benzynes (I) the *S*-level is calculated by EHT to be 1.52 eV below the *A*-level while in the 1,8-dehydronaphthalene (II) the ordering of the two levels is reversed. There is experimental evidence that I adds stereospecifically 1,4 to olefins (ethylene structure), while II adds 1,2 (anti-ethylene structure).

3. The Reaction of Methylene with Ethylene

Let us turn now to a reaction surface that has been studied in more detail, that is, the surface for the addition of methylene to ethylene (11). Figure 5 shows the various approaches of the two fragments. b) is the most symmetric approach, but the correlation diagram shows that the reaction is symmetry-forbidden for the ground configuration singlet methylene along this path. In Fig. 5c the levels have been classified as symmetric or antisymmetric with respect to the xz plane, which is the relevant symmetry element for use of the symmetry conservation rules.

The reaction surface can be constructed by EHT energy calculations, and it turns out that the methylene carbon must stay in the yz plane; there are two extreme approaches, the σ -type (5d) and the less symmetric, π -type (5e). The position of the methylene carbon can then be described by two polar coordinates in the yz plane, namely R , the distance from the center of the double bond, and an angle θ . Three eulerian angles are needed to describe the motion of the methylene fragment, assuming C—H distances and HCH angle to be fixed. If the ethylene fragment is also regarded as rigid, the description of the final stages of cyclopropane formation with rehybridization is incomplete. The situation is typ-

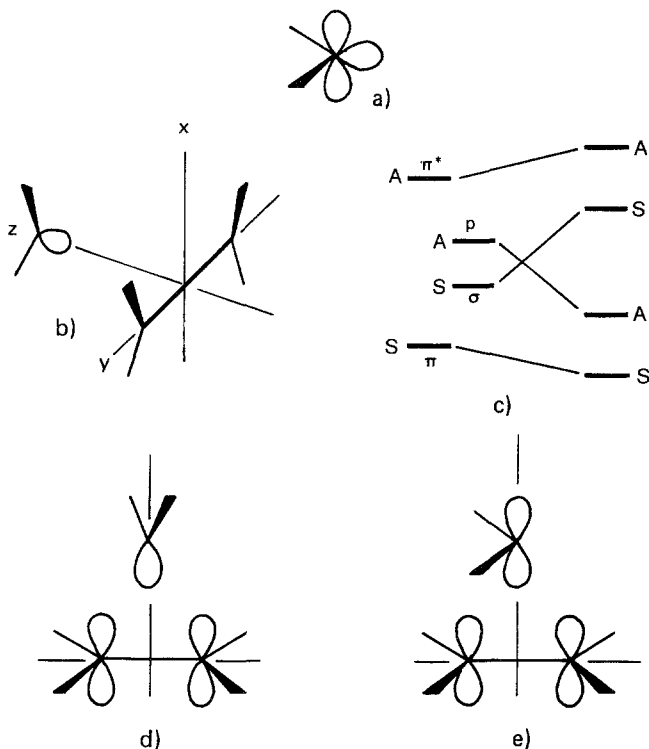


Fig. 5. a) A methylene group, showing the σ and p orbitals (HCH angle 120°). b) The most symmetric approach of methylene to ethylene. c) Level diagram for this approach. Classification of S and A refers to the plane through the midpoint of the double bond. d) Less symmetric σ approach. e) π approach.

ical of this kind of calculation; it is usually impossible to construct the full $3N-6$ -dimensional reaction surface, and relevant sections must be chosen by isolating the critical steps of the process under study.

A visualization of the approach is displayed in Fig. 6a. The positions of the methylene fragment along the reaction path are shown, the energy being minimized with respect to all parameters except the reaction coordinate, R . At large separation of the two fragments, the π -type approach is favoured, but as the separation decreases the CH_2 fragment gradually assumes the right orientation for the formation of σ -bonds with the ethylenic carbon atoms (σ -approach). One aspect of this picture should be emphasized, that is, this representation is strictly static in nature, being concerned only with the shape of the minimum-energy pathway and not with the actual trajectories on the potential energy surface.

Fig. 6b plots the variation of the energy along a purely σ -approach and along the minimum-energy approach; a considerable barrier is found for the former. The qualitative predictions of orbital symmetry match exactly the outcome of EHT calculations.

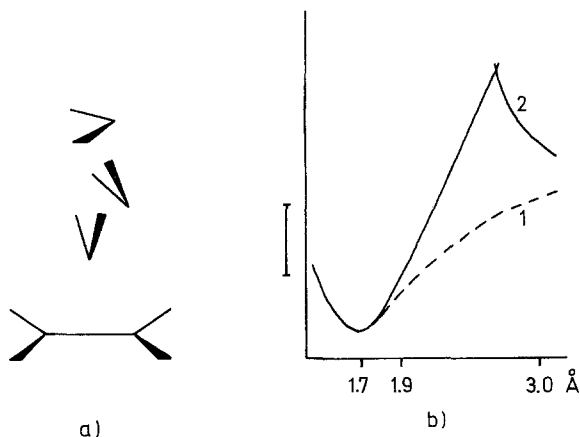
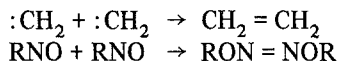


Fig. 6. a) Snapshots of methylene approaching ethylene, showing the swing from π to σ approach as the distance of the two fragments decreases. b) Energy variation along the minimum-energy path (1) and along a pure σ approach (2). The abscissa is the distance from the methylene carbon to the midpoint of the double bond. The vertical line is 0.5 eV on the ordinate energy scale.

4. Orientation of Attack and Competing Mechanisms in some other Two-Fragment Reactions

In some cases orbital symmetry rules can label the least-motion approach of two reacting fragments as forbidden. Semi-empirical MO calculations, such as EHT ones, can then be used to pick out the minimum-energy path, as outlined in the foregoing section. Another example is given by the reactions (17):



for which the correlation diagrams of Fig. 7 can be constructed.

The relevant orbitals in the dimerization of RNO are the usual four π -orbitals, plus the nonbonding lone pairs on nitrogen, that correlate with the σ and σ^* levels, thus giving rise to the crossing that makes the reaction symmetry-forbidden. The unperturbed lone pairs of oxygen are not included.

For the study of the dimerization of CH_2 , the 12-dimensional surface was reduced to a 6-dimensional one by imposing a fixed geometry on the two fragments. It was soon realized that the two carbon atoms always choose to lie in a plane bisecting both HCH angles.

Fig. 8a shows the preferred mutual orientations at large and small C-C distance, and Fig. 8b the energy variation along the least-motion and minimum-energy paths.

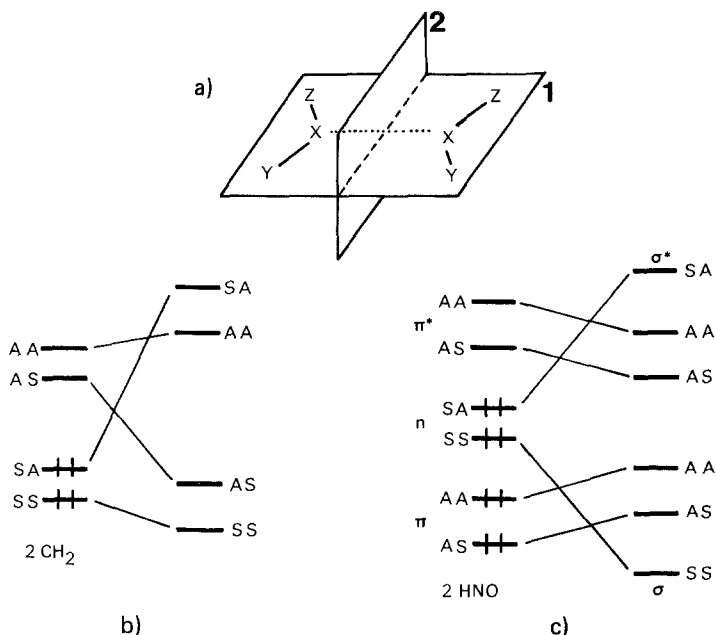


Fig. 7. Approach of two triatomic fragments. a) Relevant planes of symmetry; labels such as *AA*, *SS*, *AS* refer to symmetry or antisymmetry with respect to planes 1 and 2 respectively. b) Level diagram for the least-motion approach of two methylenes. c) Level diagram for the least-motion *cis* dimerization of HNO.

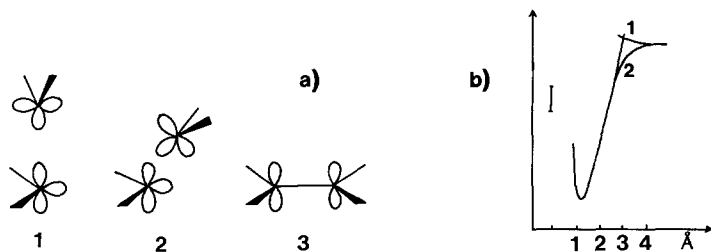
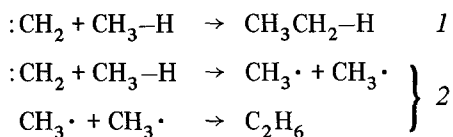


Fig. 8. a) Non-least-motion approach of two methylenes. The sequence 1–2–3 shows the mutual orientation of the two fragments with decreasing distance. b) Energy variation along the least-motion path (1) and along the least-energy path (2). The abscissa scale is the C–C distance (Å). The vertical bar is 1 eV on the ordinate energy scale.

The results for the nitroso compounds are very similar to those for the methylene dimerization. The different paths for *cis*- and *trans*-approach were explored, and optimized reaction paths similar to those shown in Fig. 8 were obtained. No activation barrier was found for any of the reactions studied. Experimental values of a few kcal/mole have been reported for the dimerization of nitroso compounds. One interesting result is that the EHT

method, in which electron repulsion is not explicitly introduced, correctly describes what in everyday language would be designated by repulsion between the lone pairs of the reactants.

The problem of relative orientation of two reacting fragments in the course of the reaction leads to the discussion of competing mechanisms, as, for instance, in the reaction of methylene with methane (18):



Whether the reaction proceed by the concerted insertion into the C–H bond as in [1] or by abstraction and recombination as in [2] depends on whether the carbon atom of the attacking methylene impinges on the C–H bond or on the hydrogen atom to be transferred:



The minimum-energy reaction path, as computed by EHT, can be visualized by the aid of snapshots of successive minimum-energy conformations of the system, although, as emphasized before, these are only representative of the infinite number of trajectories that the actual reactants can follow. Qualitative arguments in favour of an abstraction-like mechanism (indicated in Fig. 9) can be drawn from the inspection of the minimum-energy path. The barrier to migration of the hydrogen atom from methane to methylene decreases from 2.5 eV at $D = 4 \text{ \AA}$ to 0.8 eV at $D = 3 \text{ \AA}$ (D being the carbon-carbon distance); at D equal to about 2.5 \AA , the potential energy minimum associated with the hydrogen to be abstracted

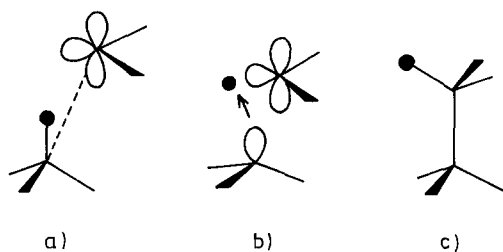


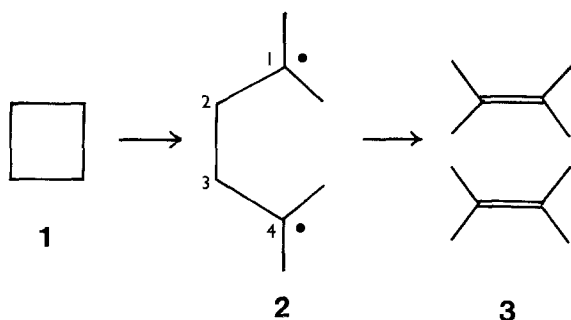
Fig. 9. Mutual orientation and interaction of methane and methylene during the reaction along the minimum-energy path. a) Initial stage: high separation. b) Intermediate stage: hydrogen migrates towards methylene. c) final stage: ethane formed. The HCH angle in methylene was tetrahedral in the calculations. The black dot is the migrating hydrogen.

vanishes, and a new minimum corresponding to the final position of this hydrogen in ethane begins to emerge. Notice that the methylene initially points its empty, electrophilic p orbital towards methane.

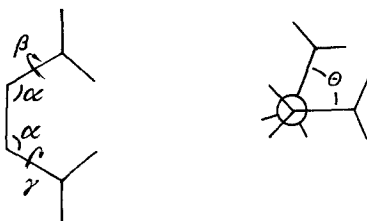
5. Tetramethylene

As the number of atoms involved in a reaction (or the number of degrees of freedom allowed to them) increases, the calculations become more and more complex, and more ingenuity is needed to isolate the essential turning points of the process under consideration.

An interesting potential energy surface that has been studied by EHT is the one for this reaction (19), in which [2], a tetramethylene diradical, is invoked as an intermediate to account for experimental facts:



The relevant internal coordinates for the ring opening are α , β , γ , and θ :



A variation of α , all the other parameters being unchanged, is a pure 1—4 stretch, during which a level crossing similar to that observed in trimethylene is found. Fig. 10 shows the energies of the A and S levels as a function of α , and a through-bond orbital coupling rationale similar to the one for trimethylene.

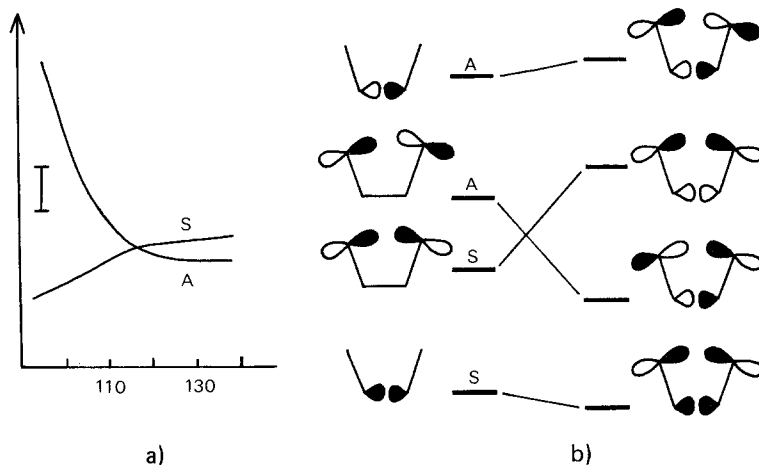


Fig. 10. a) Level crossing for increase of α (abscissa, degrees) in tetramethylene. The vertical bar is 1 eV on the energy ordinate scale. b) Level diagram for the same: through-bond coupling is shown.

Turning now to the complete four-dimensional energy surface, the crossing-point of A and S levels becomes a surface that divides a distorted cyclobutane from an unknown transient species. The calculations were carried out by varying α and θ , and by minimizing the energy with respect to β and γ at each point of the resulting grid. Fig. 11 depicts the results: the deepest minimum is for the conformation that most closely resembles cyclobutane. Past the line of level crossing, there is a flat region in which, once the optimum through-bond coupling conditions are met by proper values of β and γ , relatively unimportant steric factors produce shallow minima. That this is so was demonstrated by analogous calculations on *n*-butane, which showed a parallel behaviour. From either the “gauche” or the “trans” subminimum (Fig. 11) the products are reached without further activation energy, on lengthening the 2–3 bond.

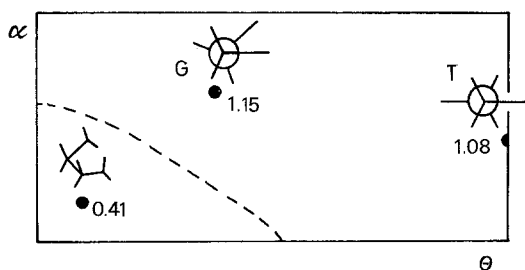


Fig. 11. Qualitative features of the α/θ potential energy surface for tetramethylene. Black dots indicate roughly the positions of the minima, with relative energies as shown (eV). G stands for “gauche”, T stands for “trans”. The dotted line is the trace of the surface of S and A level crossing. The region between G and T is flat.

From a dynamical standpoint, a broad flat region is equivalent to an intermediate, in the sense that the time spent in it by a molecule on a particular reaction trajectory is comparable to that spent in passing a transition state minimum. The word "twixtyl" was coined for the molecule in this region.

It should be noted that the theory, in this as in other cases, fails to reproduce the magnitude of the activation energy barrier and reaction heat, or even the sign of the latter. However, an *ab initio* study of the same surface (20), while extremely more expensive, gives essentially the same qualitative results as the much simpler EHT.

The tetramethylene intermediate proved to be a good model for the study (21) of the Grob fragmentation (see Fig. 12 a), the only difference being the pyramidalization at the nitrogen atom. Experiment suggests that path [1] is followed by flat molecules; the flatness is a requirement for optimum through-bond coupling, and hence A and S level crossing.

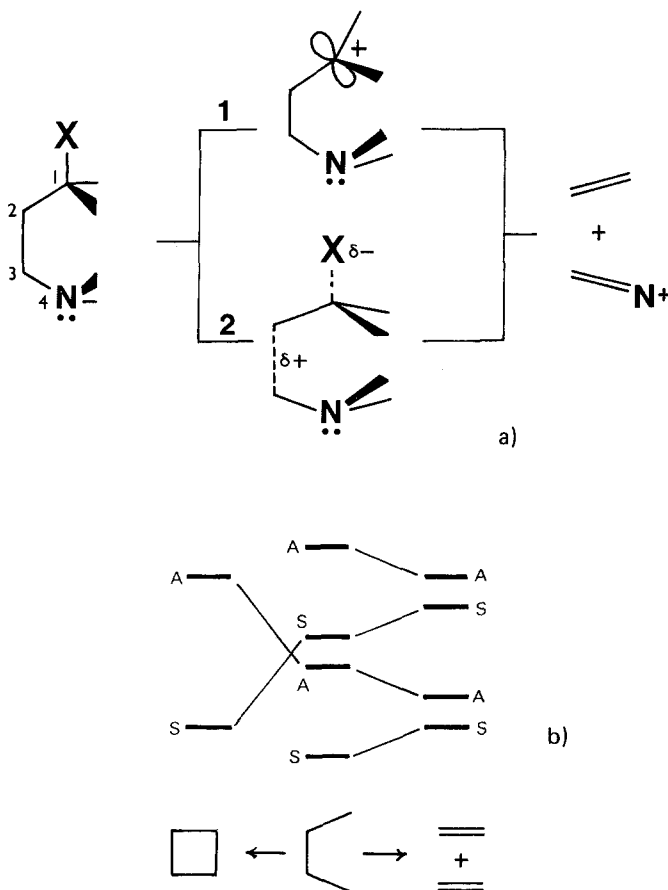


Fig. 12. a) Mechanisms for the Grob fragmentation. (1) is a two-step mechanism, (2) is a concerted single-step mechanism. b) Level diagram for the second step of path (1): fragmentation vs. reclosure.

This crossing is, in turn, an orbital symmetry requirement for the fragmentation to follow the allowed process through path [I], as shown by the level diagram of Fig. 12b.

6. Bond-Stretch Isomerism and the Reactivity of some Highly Strained Tricyclic Hydrocarbons towards Acids and Bases

Suppose that a bond, for which there is competition between through-bond and through-space orbital interaction, is a highly strained one, such as the central C–C bond in the isomerization [4] \rightleftharpoons [5]:

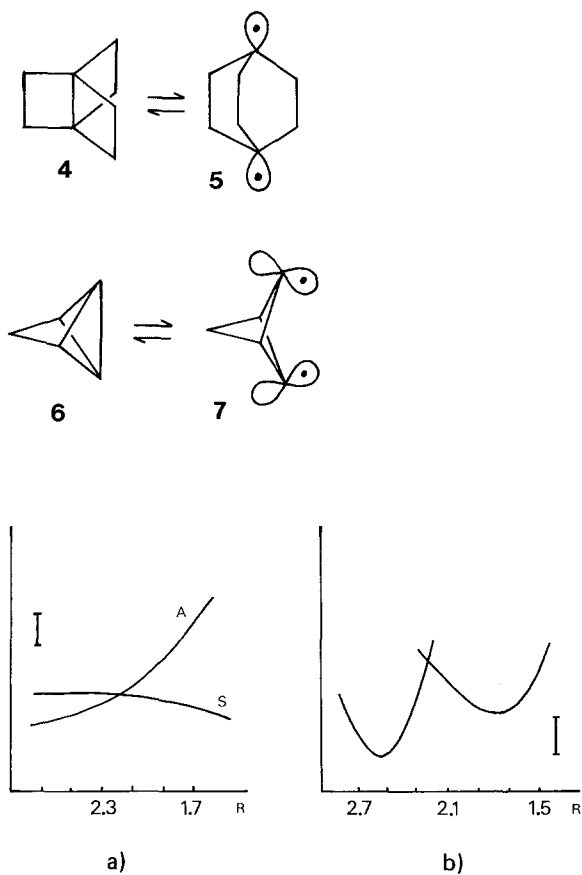
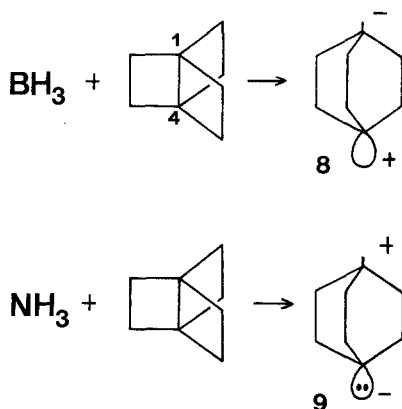


Fig. 13. Variation in energy of the frontier levels (a) and of the total energy (b) as a function of the central bond length (abscissa, Å) in the equilibrium (4) \rightleftharpoons (5). The vertical bar is 2 eV in a), 0.5 eV in b) on the ordinate energy scale.

This isomerization is a symmetry-forbidden one, since a level crossing such as the ones found in trimethylene and tetramethylene is found (22) (Fig. 13). It should be noted that, in all these cases, the two-minima structure due to level crossing might, in principle, be swept out by configuration interaction. If the barrier survives, however, the two isomers [4] and [5] can be called bond-stretch isomers. Another example is the isomerization [6] \rightleftharpoons [7] (23).

Such species should be highly reactive towards acids and bases, since they have high-lying occupied and low-lying unoccupied levels due to strain, which makes them good acceptors and donors of electrons. To test this, EHT calculations were done for the approach of BH_3 and NH_3 to [4] (22):



The 1–4 distance and the 1–B or 1–N distance were the only variables. [4] and [5] are separated by a considerable barrier. In the case of the base, three minima are present, corresponding to isomers [4] and [5] and the adduct [9]. In the case of the acid, only one minimum, that corresponding to the adduct [8], is present, since it is possible to go from [4] and [5] to [8] without any barrier. This means that on approach of BH_3 , the two species [4] and [5] merge into the zwitterion [8], i.e. acid catalyzes the isomer interconversion, while base does not.

7. Some more Complex Reaction Surfaces

The reactions of sulphur with ethylene have also been investigated by EHT (24). The geometrical framework used in this study, together with a level diagram for the reactants and thiirane, one of the products, are shown in Fig. 14.

As can be seen, the reaction of ^1D sulphur with ethylene is a symmetry-allowed one. With ethylene frozen in an idealized geometry, two minima, A and B, can be located for

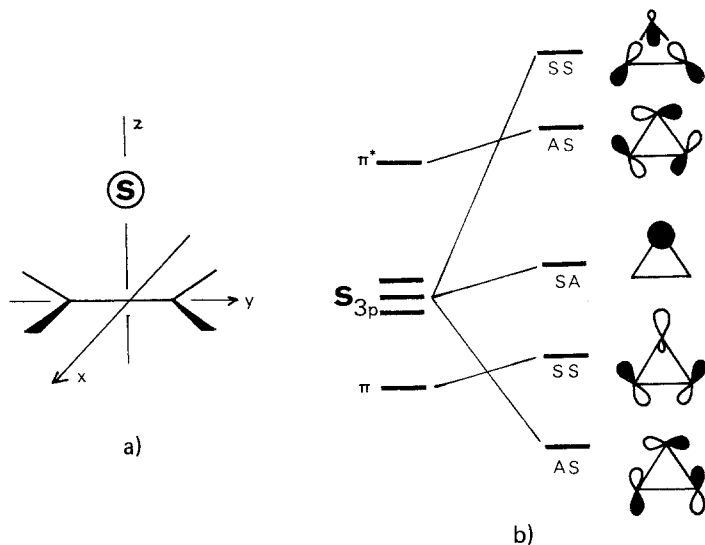


Fig. 14. a) Geometrical framework for the approach of a sulphur atom to ethylene. b) Level diagram for the same. Levels are classified with respect to reflection in the xz and yz planes.

the relative position of the sulphur atom, B being 0.8 eV above A (Fig. 15). No barrier seems to be present from infinite separation to the region of interaction. The least-motion, symmetry-allowed path leading to A is a facile one.

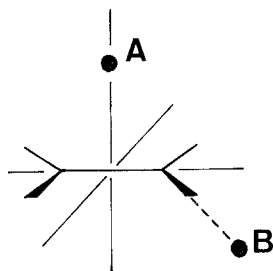
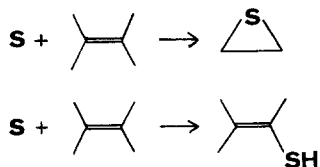


Fig. 15. The two minima for the position of the sulphur atom near an ethylene molecule. Black dots show roughly the S atom positions.

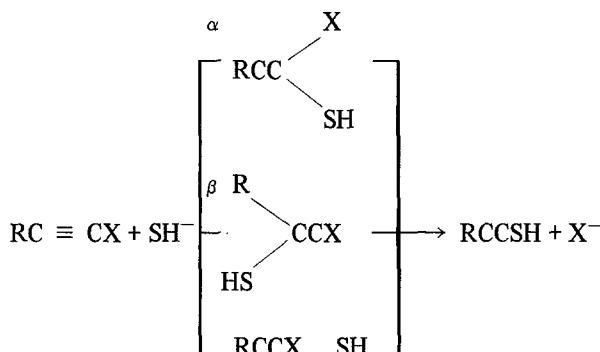
A corresponds roughly to the thiirane geometry, B corresponds to incipient insertion, since a pivoting of the S–H group in the xy plane is calculated to require no further activation energy. The two minima correspond to the two reaction mechanisms postulated from experiment:



The question arises whether the two minima correspond to two distinct, competing, concerted processes, or are connected in the multidimensional potential energy surface, so that both products stem from a common intermediate. Thorough examination of the surface in the $x = y$ plane (containing both A and B) did not reveal any path connecting the two minima without a barrier. This is a strong argument in favour of two competing processes.

The situation is different for ^3P sulphur, where only one minimum (the one leading to thiirane) is found, in complete agreement with experimental evidence.

The results obtained with the sulphur-ethylene system suggested a study of the reactions (25):



Potential energy sections were calculated for $\text{R} = \text{CH}_3$ and $\text{R} = \text{Ph}$, and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$, in the geometrical scheme shown in Fig. 16 a. The relative ease of approach of the thiolate anion in the xy plane was discussed in terms of the relative energies and positions of potential energy minima, possibly corresponding to reaction intermediates. Fig. 16 b and 16 c show, for α -attack, the positions and relative energies of these minima. No such minima were found for β -attack, while hints for a possible linear $\text{RCC}-\text{X} \dots \text{SH}$ intermediate were found for bromo- and iodophenylacetylene only. The conclusions drawn were: a) α -attack is favoured over β -attack, and b) the order of reactivity with respect to the

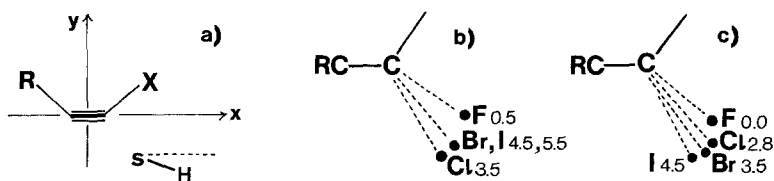
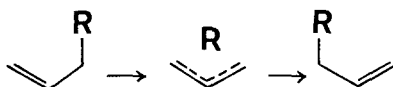


Fig. 16. a) Geometrical framework for the approach of the SH^- anion to substituted acetylenes. b) Black dots show the approximate positions of the sulphur atom for the energy minima for each halogen ($\text{R} = \text{CH}_3$). The numbers refer to the energy value of the minimum with respect to the fragments at infinite separation. c) The same as b) for $\text{R} = \text{C}_6\text{H}_5$.

leaving group is $F > Cl > Br > I$. These results are in overall agreement with the experimental evidence, which is not, however, completely unambiguous.

Application of symmetry rules also yields important results for the class of reactions known as sigmatropic shifts, in which a double bond switches position as an atom or a group migrates:



The prediction that the suprafacial path is forbidden, and the antarafacial one allowed (8) stimulated many experiments. In particular, the thermal rearrangements of the molecules shown in Fig. 17a have been studied in detail (26); here the constraints due to molecular architecture do not allow antarafacial paths, so that stereochemical mutations must take place to preserve orbital symmetry (Fig. 17b). These mutations can also be controlled by the bulk of the substituents R and R' , so that steric and symmetry factors interact in a most interesting way.

An EHT potential energy surface was calculated for the reactions summarized in Fig. 17c (27). Variation of χ provides the driving force of the reaction, since this parameter describes the swinging motion of the migrating group. In principle, this angle could assume

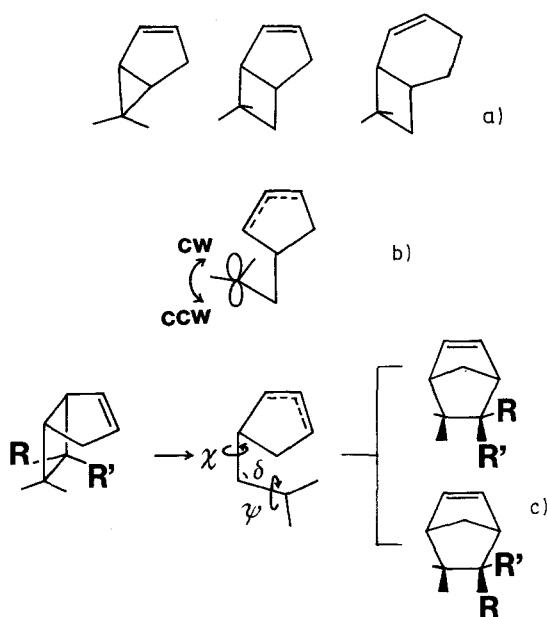


Fig. 17. a) Some interesting molecules that undergo 1–3 sigmatropic shifts. b) Clockwise (CW) and counterclockwise (CCW) rotation at the migrating center. c) Mechanisms and parameters for the EHT study of the rearrangements of bicyclo [3.2.0] heptenes with and without inversion of configuration.