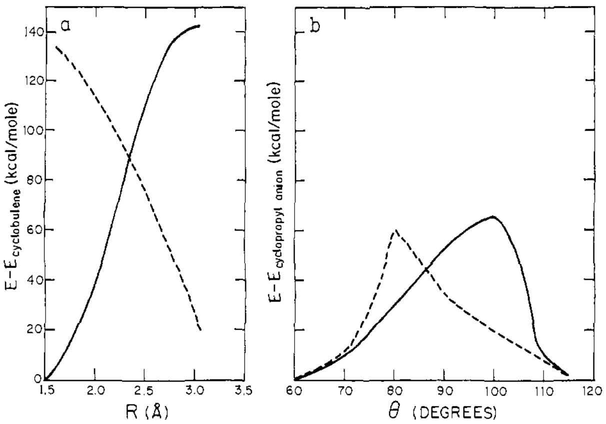

Figure 3. Plot of energy *vs.* R (a) for disrotatory electrocyclic ring opening of cyclobutene to butadiene (—) and the converse reaction (---); (b) for disrotatory electrocyclic ring opening of cyclopropyl anion to allyl anion (—) and the converse reaction (---).

reactions, the energy rises steadily to a maximum and then falls steadily, while the twist angle changes steadily throughout; in the antiaromatic reactions the energy rises all through the reaction until just before the end when it falls suddenly, while the twist angle hardly changes until just before the end of the reaction when it suddenly changes from *ca.* 0 to 90°. The sudden rotation coincides with the sudden drop in energy. These differences were obscured in the earlier work[5-9] by use of the twist angle as the reaction coordinate.

So far the antiaromatic reactions seemed quite normal; however, a very different situation arose when we tried to calculate the disrotatory ring opening of cyclobutene (**6**). As before,[1] we made the simplifying assumption that the carbon atoms are coplanar; disrotatory ring opening was enforced by setting $\phi = -\psi$ (**6**). Somewhat to our surprise, under these restraints the reaction failed to take place at all. The energy steadily increased as R increased (Figure 3a) and the twist angle remained close to zero. We then tried to study the reverse cyclization of 1,3-butadiene to cyclobutene, with the same restraints. Again the reaction failed! As R decreased, the energy rose steadily and the twist angles this time remained close to 90° (Figure 3). Evidently this is not a classical[2] reaction. The reactant and product lie in two distinct valleys lying side by side with a ridge in between, the transition state for the reaction being the lowest point in this ridge. The plot of energy *vs.* R has two minima for each value of R, corresponding to points in different valleys. Our calculations have confirmed this and lead to an estimated activation energy of 90 kcal/mol, 35 kcal/mol more than the allowed reaction.

In view of this result, and in view of the peculiar behavior of the reaction paths for the other antiaromatic reactions, we calculated the conversion of allyl cation, anion, and radical back to the corresponding cyclopropyl derivatives by the "forbidden" antiaromatic paths. In each case the backward reaction path was entirely different from the forward one, the reactions all showing "chemical hysteresis." Thus the allyl cation failed to cyclize at all to cyclopropyl cation, while the reverse paths for the cyclization of allyl anion and radical were essentially mirror images of the forward paths. In each case the energy increased steadily, and ϕ remained close to 90°, until very near the end of the reaction when the energy suddenly dropped and the methylene groups suddenly rotated through 90°. This behavior is indicated by Figure 3b.

The ridge separating the two valleys in each potential surface corresponds to an orbital crossing; it has been suggested that such a situation cannot be properly represented by a single determinant wave function and that inclusion of the lowest doubly excited configuration should lead to a large decrease in energy. This is not in fact the case. Inclusion of the lowest doubly excited configuration had little effect on the form of the potential surface for the opening of cyclobutene. The same is true of other problems where analogous orbital crossings occur, *e.g.*, rotation about the CC bond in ethylene and interconversion of valence tautomers in cyclobutadiene and planar cyclooctatetraene. In each case, we have found that inclusion of the lowest doubly excited configuration has little effect on the MINDO/2 potential energy surface.

Inclusion of CI is simply a way of taking electron correlation into account; in our semiempirical treatment this is done by adjustment of parameters so inclusion of CI as well would normally lead to an overestimate of electron correlation. Detailed studies have shown that CI needs to be introduced only in the case of isolated radical pairs formed by fission of bonds. The situation is entirely different from that in *ab initio* calculations.

These results of course invalidate previous attempts to calculate reaction paths for such reactions since earlier workers failed entirely to realize the pitfalls that awaited them. The idea that potential surfaces for reactions necessarily contain a continuous valley leading from reactants to products is clearly incorrect. No reliance can be placed on calculations based on the simple transition state picture unless, as a minimum requirement, it has been established that the forward and backward reactions follow the same reaction path.

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Classical and Nonclassical Potential Surfaces. The Significance of Antiaromaticity in Transition States

Sir:

The two preceding communications[1,2] and studies of the dimerization of ethylene[3] have shown that unexpected dangers affect attempts to calculate reaction paths by assuming that the energy of a reacting system, if minimized with respect to all other coordinates, is a one-valued function of any coordinate that varies during the reaction. Here we will consider in more detail the types of potential surface that must take part in the reactions we have considered and their

[1] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290 (1971).

[2] M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4291 (1971).

[3] M. J. S. Dewar and S. Kirschner, unpublished work.

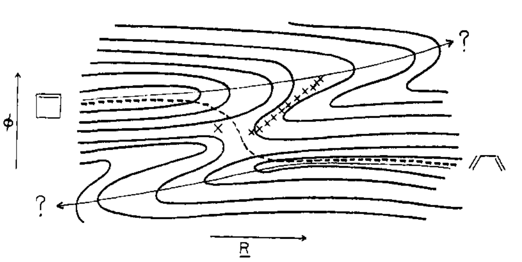
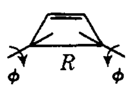


Figure 1. Schematic plot of the reaction surface for disrotatory interconversion of cyclobutene and butadiene, represented as a contour map in two dimensions (R,ϕ): "blind alley" paths are denoted by full lines and the true reaction path by a dotted line: × is the transition state. For path xxx, see text.

relationship to the mechanisms of the reactions in question.

The results[3] for the disrotatory ring opening of cyclobutene show that there are two distinct geometries that minimize the total energy for each value of the reaction coordinate R (see **1**). Points corresponding to the first geometry delineate a valley along which the twist angle of the methylene groups (ϕ; see **1**) remain close to zero, implying that they remain perpendicular to the C_4 plane. Points corresponding to the second delineate a second valley in which ϕ is close to 90°. The situation can be represented schematically by a two-dimensional contour map, R and ϕ being the coordinates (Figure 1). In our procedure, the initial geometry assumed in each calculation of the energy by our SIMPLEX minimization[1] is that for the preceding point; there is therefore no way in which one can escape from the "reactant" valley into the "product" one. To do so one would have to climb up the side of the reactant valley and cross the intervening ridge. The intervening configurations would correspond to states whose energy was *not* a minimum for given value of the reaction coordinate R.

While this argument is based solely on the results of our attempts to calculate reaction paths, and while our calculation of the potential surface corresponding to Figure 1 is incomplete, the results already obtained do show definitely that the potential surface does have this general form.



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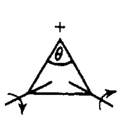
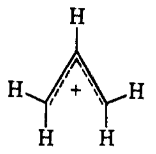


2



3

Next we have to explain the conrotatory ring opening of the cyclopropyl cation **2**. Here the reverse conrotatory cyclization of the allyl cation **3** showed the same behavior as disrotatory ring closure of 1,3-butadiene to **1**, *i.e.*, no reaction took place and the methylene groups failed to rotate (ϕ remaining near 90°); however, the forward reaction *did* take place, though in a rather spasmodic manner.

Here again there are clearly two distinct valleys as in Figure 1. In this case, however, it is eventually possible to escape from the reactant valley into the product one. One can see that it would be quite easy to circle round from high up in the reactant valley of Figure 1 to the col without going uphill by traversing the side of the valley (see the line in Figure 1 marked xxx). This unfortunately would involve backtracking to lower values of the reaction coordinate R. However a similar escape is possible, at constant R, if the reactant valley turns or has an appropriate shape (Figure 2); at ×, one can "contour" out of the reactant valley keeping θ constant and without going uphill. At this point there is a catastrophic collapse into the product valley.

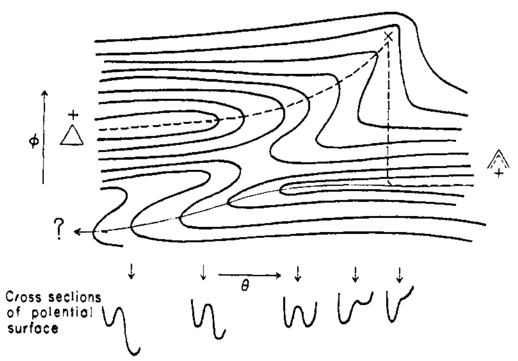


Figure 2. Schematic potential surface for conrotatory interconversion of **2** and **3**, with sections (at constant θ) indicated below: forward reaction path, ---; reverse path, —.

The other two reactions, the disrotatory interconversion of cyclopropyl and allyl anions, and the conrotatory interconversion of cyclopropyl and allyl radicals, also show "chemical hysteresis," the forward and backward paths differing; however, here both reactions do take place, albeit by "catastrophic" processes analogous to the conrotatory conversion of **2** to **3**. Again, there must be two distinct valleys but here both sides of the potential surface are analogous to the right-hand side of Figure 2.

Obviously these conjectures need confirmation by detailed calculation of the potential surfaces; such calculations are in any case essential if the transition states are to be located and their energies determined. This work is in progress. However, there remains the more interesting problem of explaining why these apparent anomalies occur—and occur *only* in the case of the antiaromatic reactions.

If the reacting system had symmetry which was conserved during the reaction, the two-valley system could be attributed to noncrossing of MO's of different symmetry. This is illustrated by the familiar[4] correlation diagram for the dimerization of ethylene *via* a rectangular transition state (Figure 3a). As long as symmetry is retained, our energy minimization procedure would lead to retention of orbital occupancy, the reaction path leading from reactants to an excited form of the product (see Figure 3a). This situation is, however, destroyed by *any* disturbance of symmetry, however small. The effect is to remove the orbital crossing so that now there is only a single unique ground state (Figure 3b). Our results cannot therefore be explained in terms of orbital symmetry, for even the "forbidden" dimerization of ethylene through a very unsymmetric transition state shows chemical hysteresis.[3]

An aromatic or antiaromatic system is by definition one for which at least two classical structures can be written. In an aromatic system, a "hybrid" of the two is more stable than either; in an antiaromatic system

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(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

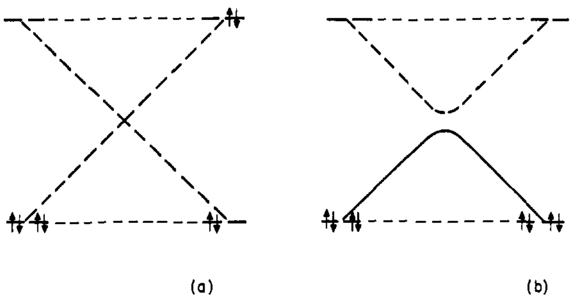

Figure 3. Orbital correlation diagram for dimerization of ethylene to cyclobutane (a) *via* a rectangular transition state; (b) *via* a trapezoidal transition state.

less stable than either. An aromatic system therefore has a unique geometry of minimum energy whereas an antiaromatic system has two distinct geometries that minimize the total energy. In accordance with Evans' principle,[5] pericyclic reactions can be divided into two classes, having their transition states isoconjugate with aromatic or with antiaromatic systems. In the former ones the transition state has a unique geometry; the valleys leading to it from reactant and product must therefore form a continuous depression in the potential surface. In the case of an antiaromatic transition state, however, there will be *two* distinct geometries of minimum energy, separated by a maximum. Since pericyclic reactions necessarily[4] involve a cyclic switching of bonds, the valley from the reactant, and the valley from the product, will lead to the two different forms of the transition state. The transition state is no longer a col separating the heads of two valleys, *i.e.* the highest point in a single continuous groove in the potential surface; here there are two grooves, each containing one of the "classical" structures for the transition state, and the transition state is the lowest point in the intervening ridge (corresponding to the high-energy degenerate "hybrid" form of the transition state). This analysis of course accounts perfectly for the potential surfaces deduced here for antiaromatic reactions; it also of course explains why it is only the antiaromatic reactions that show this anomalous behavior.

The results reported in this series of communications therefore provide further support for the interpretation of pericyclic reactions in terms of Evans' principle[5] and for their consequent classification into aromatic and antiaromatic types. There is of course no reason why an antiaromatic reaction should not be faster than an aromatic counterpart if this particular factor is outweighed by steric or other considerations. The literature shows very clearly that the use of the terms "allowed" and "forbidden" in this connection has proved misleading to organic chemists.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

(5) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 335; *Angew. Chem.*, in press.

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Alternately Pulsed Carbon-13 and Proton Magnetic Resonance, an Alternative to Nuclear Off-Resonance Decoupling

Sir:

It has been noted that when proton decoupling is terminated immediately before a field-sweep passage through the carbon-13 resonance of methyl iodide, ^{13}C–H spin coupling returns immediately, whereas reequilibration of populations of nuclear energy levels is slower, being determined by relaxation times.[1] Only small Overhauser enhancement of signal was observed. We wish to report that we have successfully modified this experiment for use together with Fourier transform carbon-13 nmr (cmr) methods[2] and that we may obtain signal improvement factors of 2.4–3.0 compared to entirely nonirradiated spectra. Furthermore, we find this alternately pulsed nmr (apnmr) technique to be a superior method for signal assignment compared to the usual off-resonance decoupling or single resonance irradiation methods.[3]

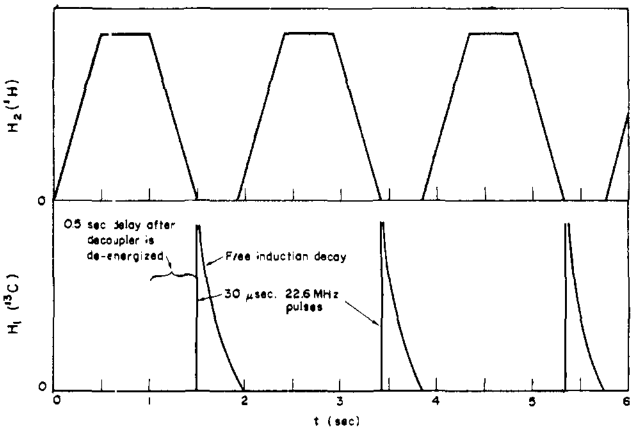

Figure 1. Pulse scheme for alternately pulsed nmr. H_1, H_2 power levels discretionary. Vertical slopes of H_2 represent rise and decay times of decoupler electronics.

Our initial alternately pulsed experiment, sketched in Figure 1, was to gate, in turn, the 90-MHz output of a broad band power amplifier (^1H spin decoupler) and the 22.6-MHz (^{13}C) pulse power amplifier of the Bruker HFX-10 nmr spectrometer, storing the ^{13}C free-induction decay (fid) in a Fabri-Tek 1080 computer. One pulse channel (B) of a Bruker Model B-KR 300 digital pulse program generator was used along with a Hewlett-Packard 10534A mixer to activate the proton decoupler for 1 sec and to terminate the pulse. A second pulse channel (C) triggered a 30-μsec ^{13}C pulse following the 0.5-sec delay found necessary to allow decoupler electronics to deenergize. This trigger voltage also initiated a 0.4-sec computer sweep for storage of the fid. This sequence was made repetitive using the pulse programmer. After 32 pulse cycles, the 1080 computer

(1) J. Feeney, D. Shaw, and P. J. S. Pauwels, *Chem. Commun.*, 554 (1970).

(2) R. R. Ernst, *Advan. Magn. Resonance*, 2, 1 (1966); R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

(3) L. D. Hall and L. F. Johnson, *Chem. Commun.*, 509 (1969); H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 1355 (1969); F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, 60, 1152 (1965); L. D. Hall and L. F. Johnson, *Chem. Commun.*, 509 (1969).