energy for rearrangement of **1** (25 kcal/mol) is unfortunately rather large.

Cyclobutene (4). In our preliminary calculations we assumed the carbon atoms in cyclobutene to be coplanar; the geometry of each point along the reaction was optimized subject to this condition. The reaction then followed a normal conrotatory path, in agreement with qualitative predictions[1-4] and experiment. The calculated activation energy (90 kcal/mol) was, however, considerably greater than that (36 kcal/mol) observed for 3,4-dimethylcyclobutene.[22] Further study showed that the major part of this discrepancy was due to the assumption of coplanarity; as one might expect, twisting of the molecule (see **7**) has a stabilizing effect on the intermediate phases of the reaction. Our latest estimate of the activation energy, placing no restraints on the reaction, is 55 kcal/mol. While part of the remaining discrepancy may have been due to the effect of the methyl substituents, the major factor undoubtedly is the known tendency of MINDO/2 to overestimate the stability of four-membered rings.

Finally it should be noted that these reactions all seem to be normal "classical" processes. The calculated reaction paths for the reverse reactions agree with the forward ones within the limits of accuracy of the computation and the geometry changes steadily during each reaction. In particular, the methylene groups rotate in unison and steadily throughout.

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

[22] H. M. Frey and R. F. Skinner, *Trans. Faraday Soc.*, **61**, 1918 (1965).

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MINDO/2 Study of Antiaromatic ("Forbidden") Electrocyclic Processes

Sir:

The preceding communication[1] described MINDO/2 calculations of "classical"[2] reaction paths for the electrocyclic ring opening of cyclopropyl cation (**1**), anion (**2**), and radical (**3**), and of cyclobutene (**4**). All these reactions are predicted to follow "allowed"[3] paths *via* aromatic[4] transition states. These conclusions are of course well known experimentally; the main interest in calculations of this kind lies rather in the possibility of estimating the extent to which the "aromatic" reactions are favored over the analogous antiaromatic ("forbidden"[3]) ones.

In order to force the reactions to follow a forbidden path we constrained the twist angles (ϕ, ψ) of the methylene groups (see **5**, **6**), initially zero, to remain equal in magnitude, and of the same sign for conrotatory processes and opposite sign for disrotatory ones. The calculations otherwise followed the same procedure as before,[1] the apical angle (θ) of cyclopropyl (**5**), or the length (R) of the breaking σ bond in **4** (see **6**) being taken as reaction coordinates.

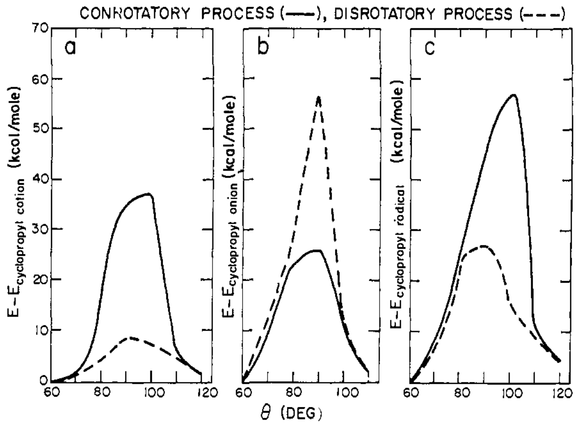


Figure 1. Plot of energy *vs.* θ for rearrangement of the cyclopropyl (a) cation, (b) anion, and (c) radical.

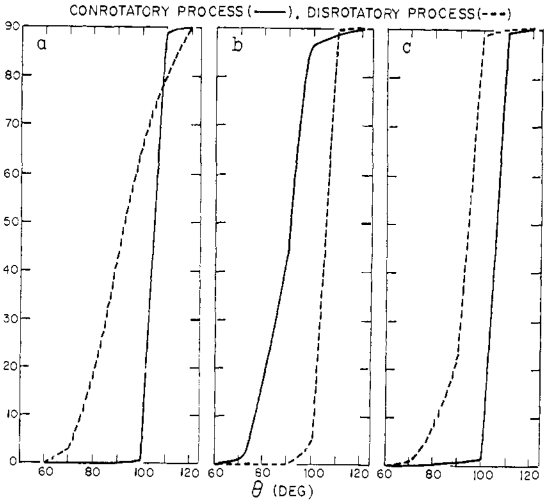
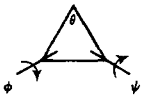


Figure 2. Plot of ϕ ($= \pm\psi$) *vs.* θ for rearrangement of the cyclopropyl (a) cation, (b) anion, and (c) radical.



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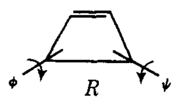

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Figure 1 compares the reaction paths for the aromatic and antiaromatic rearrangements of **1–3** while Figure 2 shows a corresponding plot of the twist angle ϕ ($= \pm\psi$) *vs.* θ. The differences in activation energy between the aromatic and antiaromatic rearrangements of **1**, **2**, and **3** are, respectively, 30.6, 35.0, and 27.6 kcal/mol, the values for **1** and **2** being in fair agreement with earlier calculations.[5-9]

The plots for the aromatic and antiaromatic reactions are clearly quite different in type. In the aromatic

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

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

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

[4] M. J. S. Dewar, *Angew. Chem.*, in press; *Tetrahedron, Suppl.*, **8** (1), 75 (1966); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 325.

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[8] D. T. Clark and G. Smale, *Tetrahedron Lett.*, 3673 (1968).

[9] D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969).

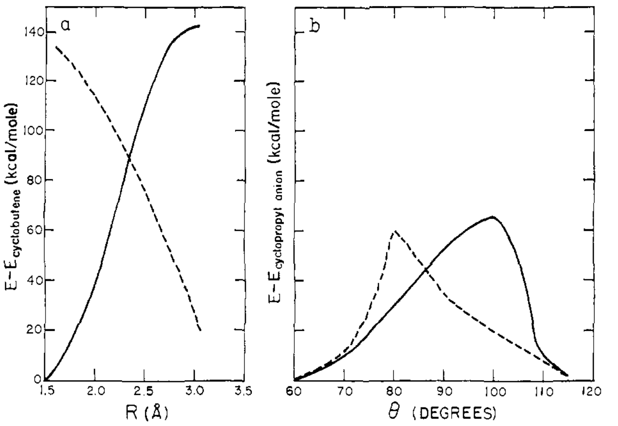

Figure 3. Plot of energy *vs.* *R* (a) for disrotatory electrocyclic ring opening of cyclobutene to butadiene (—) and the converse reaction (---); (b) for disrotatory electrocyclic ring opening of cyclopropyl anion to allyl anion (—) and the converse reaction (---).

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

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[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.