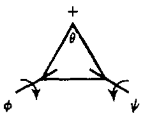
Communications to the Editor

MINDO/2 Study of Aromatic ("Allowed") Electrocyclic Reactions of Cyclopropyl and Cyclobutene

Sir:

Electrocyclic reactions are of especial interest since it was a process of this kind that initiated the classic studies of Woodward and Hoffmann.[1] The experimental facts are now well known and several theoretical treatments have appeared.[1-12] Here we report a study of the electrocyclic ring opening of cyclopropyl cation, anion, and radical (**1**–**3**) and of cyclobutene (**4**), using the MINDO/2 method,[13,14] with modified parameters[15] that give better estimates of molecular geometries, in particular CH bond lengths. In **1**–**3**, the reaction coordinate was taken to be the apical angle θ (see **1**), in **4** the length (R) of the bond undergoing rupture. The reaction path was calculated for successive increments of the reaction coordinate; the geometry at each point was calculated by an iterative procedure using a program (SIMPLEX) written by Dr. A. Brown and modified by Dr. D. H. Lo, the initial gometry being that for the previous point.



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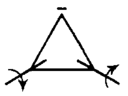

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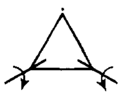

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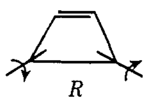

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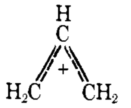
Cyclopropyl Cation (1). We predict the ring opening to be disrotatory, in agreement with qualitative theories,[1-4] experiment,[16] and calculations by EH,[6] CNDO/2 (with CI),[5] and *ab initio* SCF[7] methods.

We predict the reaction to require activation, in disagreement with the EH[6] and *ab initio*[7] results; no value was quoted in ref 5. At first sight this may seem to be at variance with the evidence[16] that rearrangement of the nascent cyclopropyl cation acts as a driving force in the solvolysis of cyclopropyl esters; here, however, the nascent cation is formed with a pyramidal geometry at the cationic center and our calculations indicate that such an ion should rearrange without activation by the observed[16] disrotatory path. Indeed, we predict the transition state for rearrangement of planar cyclopropyl ion to show a corresponding distortion from planarity of the cationic center.

Our calculations lead to the definite prediction that *free* **1** should be a stable species. This indeed appears to be the case, judging by the isolation of small amounts of intact cyclopropyl derivatives by the deamination of *cis*- and *trans*-2-phenyl-1-cyclopropylamine.[17] The fact that both isomers gave similar mixtures of *cis*- and *trans*-2-phenylcyclopropyl derivatives indicates that the reactions forming them were of S_N1 type.

It is possible that the discrepancy with Clark and Armstrong's[7] results may have been due to their use of an assumed geometry for the cyclopropyl cation, leading to an overestimate of its energy. Equally, our estimate of the activation energy is probably too large since MINDO/2 underestimates strain energies and so overestimates the stability of cyclopropyl cation.



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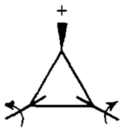

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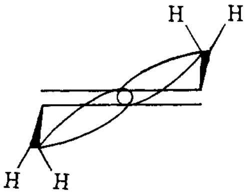

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Cyclopropyl Anion (2). Here conrotatory ring opening is predicted, again in agreement with theory,[1-4] experiment,[1] and CNDO/2[8] and *ab initio*[9] calculations. The predicted activation energy (31 kcal/mol) also agrees reasonably well with the earlier estimates.[8,9] In **2**, the carbanion center is predicted to be nonplanar (*cf.* ref 18); during the reaction, the methine proton moves progressively into the C_3 plane.

Cyclopropyl Radical (3). Ring opening here is predicted to be *disrotatory*, in direct contradiction to EH calculations.[19] In this case no conclusions can be drawn from qualitative arguments based on first-order theory;[1-4] thus, the transition state is isoconjugate with cyclopropenyl radical which is predicted to be nonaromatic by the PMO method.[4] Recent experimental work[20] has, however, shown that Hückel $(4n + 3)$ radicals are probably aromatic, a conclusion supported[21] by SCF calculations. On this basis one would expect the transition state for **3** to be of the Hückel[4] type, corresponding to disrotatory ring opening. An experimental test of this prediction is obviously highly desirable; the calculated activation

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

(2) H. C. Longuet-Higgins and F. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(3) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966).

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

(5) D. T. Clark and G. Smale, *Tetrahedron*, **25**, 13 (1969).

(6) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).

(7) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969).

(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).

(10) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(11) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

(12) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **40**, 2018 (1967).

(13) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(14) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(15) M. J. S. Dewar, D. H. Lo, and N. Bodor, in preparation.

(16) P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966).

(17) W. Kirmse and H. Schütte, *ibid.*, **89**, 1284 (1967). This conclusion is also in agreement with recent work by Professor P. von R. Schleyer (personal communication).

(18) M. J. S. Dewar and M. Shanshal, *J. Chem. Soc. A*, 25 (1971).

(19) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(20) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *ibid.*, **91**, 2823 (1969).

(21) C. G. Venier, unpublished work.

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.

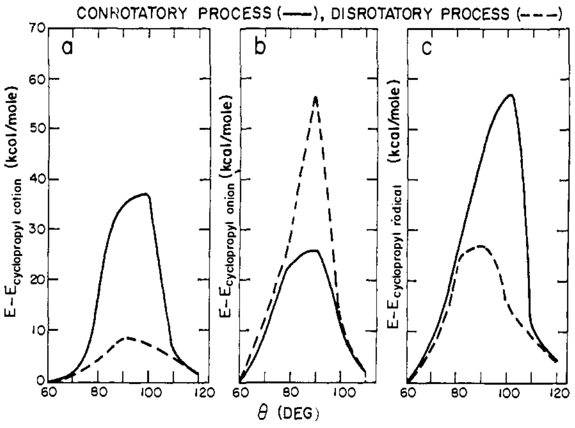


Figure 1. Plot of energy *vs.* θ for rearrangement of the cyclopropyl (a) cation, (b) anion, and (c) radical.

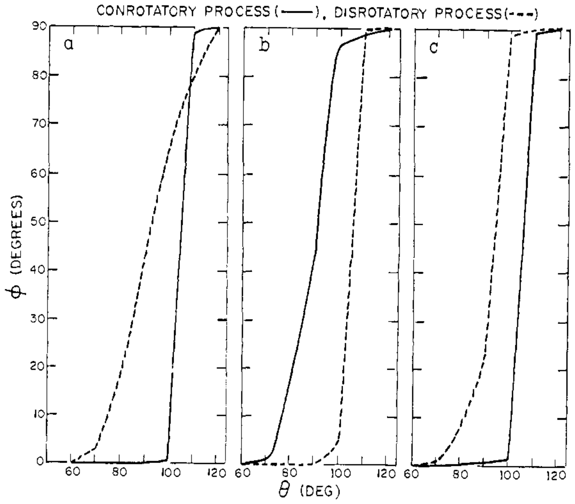
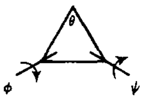


Figure 2. Plot of ϕ ($= \pm\psi$) *vs.* θ for rearrangement of the cyclopropyl (a) cation, (b) anion, and (c) radical.



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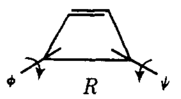

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Figure 1 compares the reaction paths for the aromatic and antiaromatic rearrangements of **1–3** while Figure 2 shows a corresponding plot of the twist angle ϕ ($= \pm\psi$) *vs.* θ. The differences in activation energy between the aromatic and antiaromatic 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.

(5) D. T. Clark and G.Smale, *Tetrahedron*, **25**, 13 (1969).

(6) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).

(7) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969).

(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).