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A SIMPLE THEORETICAL MODEL FOR PREDICTING THE EFFECTS OF BENZANNELATION AND BISMETHYLENATION ON THE RATES OF FOUR-MEMBERED RING-OPENING REACTIONS

CHARLES F. WILCOX, JR. and BARRY K. CARPENTER*
Department of Chemistry, Cornell University, Ithaca, NY 14853, U.S.A.

and

WILLIAM R. DOLBIER, JR.
Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

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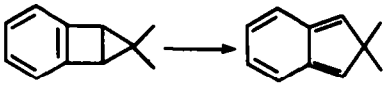
Abstract—A model based on simple Hückel MO theory is applied to the ring-openings of several cyclobutene derivatives and their benzo- and bis-methylene-analogs. The calculated changes in activation enthalpy upon benzannelation and bismethylenation are found to be in qualitative accord with experimental results. Application of the model to Dewar benzene and bicyclo[4.2.0]octa-2,4,7-triene ring-opening is discussed.

The concept of thermodynamic driving force has long been used to interpret rates of chemical reactions. Thus it is an empirical observation that, within a series of similar reactions, the most exothermic process will usually have the lowest activation enthalpy. However there are notable exceptions to this rule, perhaps the most important being reactions that are exothermic but forbidden by the principle of orbital symmetry conservation.[1] In such cases the lack of direct correlation between electronic groundstates of the reactant and product results in a special destabilization of the transition state. For example, the thermal conversion of bicyclo[2.2.0]hex-2-ene to cyclohexa-1,3-diene occurs with an activation enthalpy greater than that for the ring-opening of cyclobutene,[2a,b] despite the fact that the former reaction is more exothermic by about 27 kcal/mol.[2c]

In this connection it is interesting to compare the activation enthalpies for the ring-opening of the pseudoindene 1 and bicyclo[2.1.0]pentene (2).[2b,d]



1

$\Delta H^{\ddagger}$ (obs.)

18.4 kcal/mol

2

26.2 kcal/mol

The thermodynamic driving force argument leads to the conclusion that the aromatic stabilization lost by ring-opening of 1 should result in a higher activation enthalpy than for the corresponding transformation of 2. In fact the converse is found experimentally.[2d] In this case it is not clear how to resolve the problem by orbital symmetry arguments, since both reactions are formally forbidden 4n electron disrotatory processes.

The purpose of the present work is to describe a simple model that can be used to rationalize this result and to predict the effect of benzannelation or bismethylenation on the rates of other 4-membered ring-opening reactions.

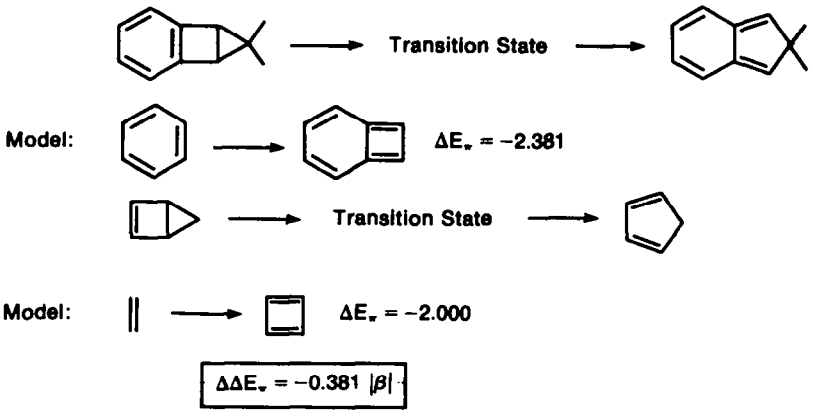
In the belief that the phenomenon may have a topological basis,[3] we have employed a technique which relies almost exclusively on orbital topology for its predictions—simple Hückel MO theory. The model transition state employed for calculations on the disrotatory ring-opening is the π-isoconjugate[4a] hydrocarbon of Hückel topology[4b] while for the conrotatory process the corresponding Möbius topology[4b] is used. This type of model has recently been shown to be of use in the analysis of substituent effects on the rates of pericyclic reactions.[3]

Application of the technique to the specific problem of determining the effect of benzannelation on cyclobutene ring-openings is shown in Fig. 1.

For each reaction the difference in π-electron energy (calculated by the HMO method) between the model reactant and model transition state is recorded as ΔE_{π} (in absolute β units). Where the cyclobutene is monocyclic (not counting any benzene rings) we have presumed that the reaction will follow a conrotatory pathway, in accord with experimental results[5a,b] and the rules of conservation of orbital symmetry.[1] In addition one may note that this is the pathway with the more negative ΔE_{π}, as expected.[4a,b] For the bicyclic systems we assume that geometrical constraints will force a disrotatory ring opening. Such an assumption may not always be valid when the saturated ring is five-membered or larger, but is probably secure for the 3- and 4-membered rings considered in the present work.

The Möbius cyclobutadiene and Möbius benzocyclobutadiene used as models for the conrotation transition states are identical with their more familiar Hückel

Disrotatory openings:



Conrotatory openings:

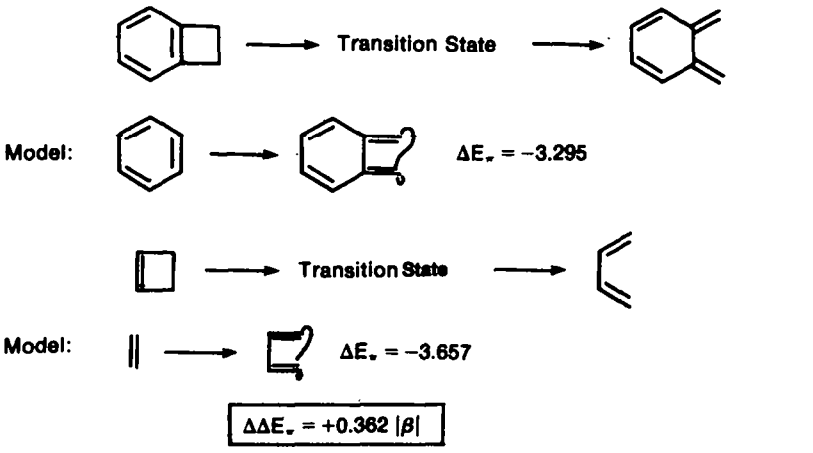


Fig. 1.

analogs except that the breaking bond (a σ bond in the reactant) is given a resonance integral of opposite sign to that used for the normal in-phase overlap.[6]

The most striking observation is that benzannelation is predicted to decrease the activation enthalpy for disrotatory ring-opening (negative $\Delta\Delta E_\pi$) but to increase the activation enthalpy for conrotatory ring-opening (positive $\Delta\Delta E_\pi$). As shown in Table 1, one finds that this prediction receives experimental support and is, furthermore, reflected even more strongly in the bismethylenecyclobutanes.

For the parent monocyclic bismethylenecyclobutane the Hückel/Möbius procedure shows a clear preference (lower ΔE_π) for the conrotatory ring-opening. By contrast the correlation-diagram approach is unable to make a prediction owing to the orbital degeneracy of the tetramethyleneethane biradical.[8] The predicted conrotation appears to receive experimental support in the work of Gajewski.[9]

The ratio of $\Delta\Delta H^\ddagger$ to $\Delta\Delta E_\pi$ is found to be surprisingly constant (Table 1) and within the range of values of $|\beta| = 15$–55 kcal/mol commonly used to correlate chemical and physical phenomena.[10] It is not clear whether this approximately linear relationship between $\Delta\Delta H^\ddagger$ and $\Delta\Delta E_\pi$ is fortuitous or whether the model used in our calculations is in fact sufficiently accurate to allow semiquantitative estimation of differences in activation enthalpy. We are currently investigating this question.

It is instructive to consider the effect of annelation with polyacenes in place of a simple benzene ring. For example, one can analyze the disrotatory ring-opening of the naphtho-analogs of pseudoindene 1 very simply. Since the Hückel π-electron energies of 3 and 4 are identical, their predicted relative rates of ring-opening will depend only on the π-electron energies of the transition state models 5 and 6.

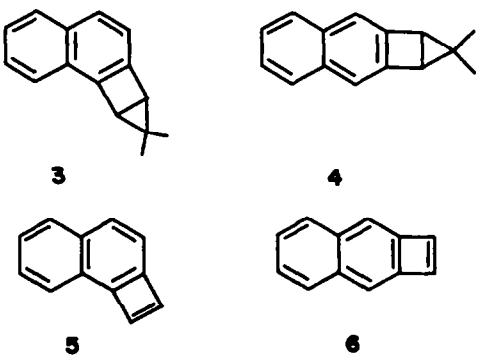
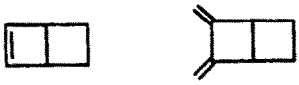
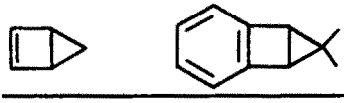


Table 1.

	Reaction Stereochemistry	$\Delta\Delta E_\pi$[a]	$\Delta\Delta H^\ddagger$[b]	$\Delta\Delta H^\ddagger/\Delta\Delta E_\pi$
	Conrotation	0.611	14.1	23.1
	Disrotation	-0.736	-14.7	20.0
	Conrotation	0.362	~ 6.5[c]	~18
	Disrotation	-0.381	- 7.8	20.5

[a] ΔE_π is the difference in Hückel π-electron energy (in absolute β units) for the reactant and model transition state. $\Delta\Delta E_\pi$ is the difference in ΔE_π for the two molecules shown in each line.

[b] $\Delta\Delta H^\ddagger$ is the difference in observed activation enthalpy for the ring opening reactions (units are kcal/mol). Data from references 2a, 2b and 7a–c.

[c] Calculated from the data in reference 7c with the assumptions that ring-opening is rate determining and that $\Delta S^\ddagger$ is equal to that for the conversion of cyclobutene to butadiene.

A general method for determining the relative stabilities of 4n membered rings of this type has already been described.[11] In the particular example considered here a lower energy is expected for **6**, leading to the prediction of a more facile ring-opening for **4** than for **3** (despite the fact that **4** probably leads to the less stable product).

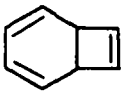
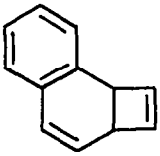
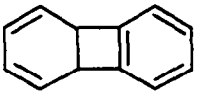
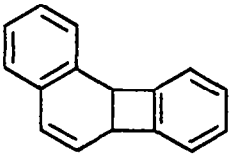
Application of the model to the (presumed disrotatory) ring-opening of benzannelated bicyclo[4.2.0]octatrienes results in a number of interesting predictions, summarized in Table 2. It is is intriguing to find that the activation enthalpy for the ring-opening of bicyclo[4.2.0]octatriene is predicted to increase upon benzannelation of the 6-membered ring but to decrease upon benzannelation of the 4-membered ring. If the semiquantitative correlation between $\Delta\Delta E_\pi$ and $\Delta\Delta H^\ddagger$ outlined in Table 1 is genuine then the $\Delta\Delta E_\pi$ values calculated for compounds **8–10** can be converted to $\Delta\Delta H^\ddagger$ values and thence, using the known activation parameters for the ring-opening of the parent (**7**),[12] to $\Delta H^\ddagger$ values. These are listed in Table 2. To our knowledge there are no quantitative data on the rates of ring opening of **8–10** in the literature, however the qualitative observations that **10** can be isolated as a stable compound from the dimerization of benzocyclobutadiene[13] whereas **9** appears to suffer facile ring opening at 45°[14] are certainly in accord with our predictions, although we emphasize that our calculations apply only to the disrotatory mode.

Application of the theoretical model to the ring-opening of Dewar benzene is an intriguing prospect in view of the recent intense interest in the mechanism of this reaction.[15a–c] In particular, there is compelling experimental evidence for the involvement of electronic excited states,[15a] although their quantitative importance in the overall transformation is not yet known.[15c] One can anticipate that our groundstate model would be unable to predict the effects of benzannelation or bis-methylenation on the activation enthalpy for ring-opening if, in fact, the excited state pathway were significant. This is found to be the case. For example the calculations predict a higher activation enthalpy for the ring-opening of 5,6-bis-methylenebicyclo[2.2.0]hex-2-ene than for Dewar benzene, whereas the converse is observed experimentally.[16] Remarkably, however, if we use an excited state model in which the transition state for each reaction is presumed to possess a pair of singly occupied molecular orbitals a good qualitative correlation between $\Delta\Delta E_\pi$ and $\Delta\Delta H^\ddagger$ is observed (Table 3).

Again one must recognize that the correlation between $\Delta\Delta E_\pi$(E.S.) and $\Delta\Delta H^\ddagger$ could be fortuitous, especially since attempts to detect excited state anthracene from the thermolysis of its Dewar valence isomer were unsuccessful.[17b] Nevertheless, the failure of the groundstate model to even qualitatively predict the results is certainly suggestive of the incursion of some other mechanism.

Looking ahead, we see no reason to believe that the contrasting effects of benzannelation on the rates of allowed and forbidden reactions should be restricted to cyclobutene ring-openings. It is possible that the effects

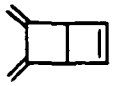
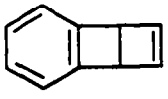
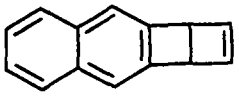
Table 2. Predicted effect of benzannelation on the rate of the bicyclo[4.2.0]-octatriene to cyclooctatetraene conversion

		$\Delta\Delta E_\pi$[a]	$\Delta H^\ddagger$ predicted[b]
7		[0.000]	[18.1]
8		0.338	25
9		-0.124	16
10		0.168	22

[a] Difference in ΔE_π for disrotatory opening of the indicated compound and the parent bicyclo[4.2.0]octatriene.

[b] Enthalpy of activation (kcal/mol) predicted from $\Delta\Delta H^\ddagger \simeq 20.4\ \Delta\Delta E_\pi$ and from $\Delta H^\ddagger$ for the parent compound, 7 (calculated from the data in reference 12).

Table 3.

		$\Delta\Delta E_\pi$(G.S.)[a]	$\Delta\Delta E_\pi$(E.S.)[b]	$\Delta\Delta H^\ddagger$(obs)[c]
		0.611	-0.222	-5.8
		0.362	0.074	~0[d]
		0.427	0.170	2.0

[a] $\Delta\Delta E_\pi$ for electronic groundstates.

[b] $\Delta\Delta E_\pi$ using a singly excited configuration for the transition state.

[c] Data obtained from references 16, 17a, 17b.

[d] Calculated from data in reference 17a with the assumption that $\Delta S^\ddagger$ is equal to that for the ring-opening of Dewar benzene.[18]

discussed in this paper are just manifestations of a more general phenomenon which applies to pericyclic reactions as a whole.

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[4a]M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*. Plenum, New York (1975); [b]H. E. Zimmerman, *Accts. Chem. Res.* **4**, 272 (1971).

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[6]In an annelated Möbius cyclobutadiene the phase discontinuity can occur across any of the π bonds of the 4-membered ring, except the one shared by the two rings, without changing the HMO π-electron energy. This can be seen intuitively by following the arguments of Zimmerman[4b] but can be proven rigorously by application of Sachs' theorem (for discussion of which see I. Gutman and N. Trinajstic, *Topics Curr. Chem.* **42**, 49 (1973).

[7a]1,2-Bismethylenecyclobutane: W. von E. Doering and W. R. Dolbier, Jr., *J. Am. Chem. Soc.* **89**, 4534 (1967); [b]2,3-Bismethylenebicyclo[2.2.0]hexane: C.-S. Chang and N. L. Bauld, *Ibid.* **94**, 7593 (1972); [c]Benzocyclobutene: F. R. Jensen, W. E. Coleman and A. J. Berlin, *Tetrahedron Letters* 15 (1962).

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[18]*Note added in proof.* Following submission of this paper, an experimental determination of the activation enthalpy for ring-opening of Dewar naphthalene has been reported. The value of $\Delta H^{\ddagger}$ is virtually identical to that for ring-opening of Dewar benzene, as we hypothesized: W. Grimme and U. Heinze, *Chem Ber.* **111**, 2563 (1978).