inversion in XIV occurs in breaking an oxygen–oxygen single bond in a transoid fashion.

7. Conclusions

Because more than one electronic surface is inevitably involved in photochemical reactions, it is desirable to phenomenologically classify photochemical reactions prior to developing mechanistic interpretations. Our mechanistic understanding of a given reaction will depend to a considerable extent on whether the reaction (1) occurs entirely on an excited state surface, X type, (2) starts on an excited surface and results in bond breaking to give ground-state nonbonding radical intermediates which subsequently react, N type; or (3) starts on an excited surface and ends in a bonding ground state without the intervention of intermediates (or the reverse), G type. We have indicated the ways in which first-order perturbation theory and an analysis of the breakdown of the Born–Oppenheimer approximation can be used to develop a mechanistic understanding of the three types of photochemical reactions.

The PMO treatment offers a direct insight into the driving force for G-type photochemical pericyclic reactions, whereas an orbital symmetry analysis offers very little insight into the virtue of concertedness for these processes. Even Lewis's principle of maximum bonding in the transition state[55] is difficult to apply to photochemical processes in the absence of an electronic analysis coupled with an analysis of Born–Oppenheimer breakdown. The discussion in section 4 indicates that in reactions that proceed through orbitally degenerate structures, where there are significant symmetry elements, those elements will be destroyed by electronic–vibronic coupling. This is the specific mechanism for conversion of electronic excitation to chemical potential for those reactions.

Finally, it appears that chemical reactions generally might be usefully divided into two types: those for which the Bell–Evans–Polanyi analysis holds (BEP reactions) (see section 2) and those for which it does not (anti-BEP reactions). For the BEP reactions both thermal and photochemical processes will proceed by paths which minimize the energy gap between the ground state and the first excited state. The anti-BEP reactions will proceed by paths which maximize that same gap.

Acknowledgments. It is a pleasure to acknowledge the patient help and criticism of Professor William Rhodes in the development of this manuscript. I am also indebted to many of my colleagues, the editor, and referees for numerous helpful suggestions.

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Ground States of σ-Bonded Molecules. XIV.[1a] Application of Energy Partitioning to the MINDO/2 Method and a Study of the Cope Rearrangement[1b]

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Abstract: The technique of energy partitioning of Fischer and Kollmar has been extended to the MINDO/2 approximation and used in a detailed analysis of the Cope rearrangements of 1,5-hexadiene, bullvalene, barbaralane, and semibullvalene. The relationship between the quantities introduced in this treatment and bond lengths and bond energies is studied.

One of the problems that has arisen with the development of more sophisticated MO treatments[3] is the difficulty of relating the results of such calculations to the traditional picture of molecules in terms of localized bonds, resonance energy, etc. Correlations of this kind were well established in the HMO era;[4] however, SCF expressions for the total energy[5] are far more complex and it is very much harder to see their relationship[6] to traditional ideas.

Recently Fischer and Kollmar[7] have proposed a scheme for dissecting such expressions into contributions by individual atoms and bonds. Such a partitioning of the energy is clearly just what is needed to interpret and enlarge on the classical bond picture; it also provides an excellent basis for studying the effect of changes in the parameters in semiempirical SCF–MO treatments.

We have been applying this technique to the MINDO/2 approximation,[8,9] with both objects in view.

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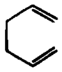
In its present form the method suffers from several deficiencies; a study by energy partitioning will, we hope, provide a guide to an improved set of parameters. MINDO/2 has also been applied with considerable success to the calculation of reaction paths and activation energies for a number of reactions; here such an analysis should provide a clue to the relationship between structure and reactivity.

One reaction in which MINDO/2 has been particularly successful is the Cope rearrangement. It correctly predicted that biallyl (**1**)[10] should rearrange preferentially *via* the chair-type transition state (**2**), rather than the boat-type transition state (**3**); it also correctly predicted that bullvalene (**4**), barbaralane (**5**), and semibullvalene (**6**)[11] should rearrange much more easily than **1**, and in that order of increasing reactivity, even though the transition states are perforce derivatives of **3** rather than **2**.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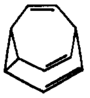
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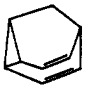
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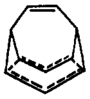
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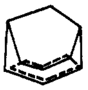
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The reason for these variations in activation energy seemed an interesting subject for analysis by energy partitioning, the more so since Simonetta, *et al.*,[12] have recently published an analogous study of the rearrangement of **7** using the CNDO/2 method and since certain of their conclusions seemed surprising. Here we report an analysis of the MINDO/2 calculations for **1**, **4**, **5**, and **6**.

Theory

In the INDO approximation,[13] the basis of MINDO/2, the total energy (E) of a molecule can be expressed as a sum of one-center terms (E_A) and two-center terms (E_{AB}).

$$E = \sum_{A} E_A + \sum\sum_{A<B} E_{AB} \tag{1}$$

(a) Monocentric Terms. The monocentric terms E_A can in turn be expanded in terms of one-center core attraction terms ($E_A{}^U$), coulomb terms ($E_A{}^J$), and exchange terms ($E_A{}^K$). These can in turn be expressed

$$E_A = E_A{}^U + E_A{}^J + E_A{}^K \tag{2}$$

in terms of standard integrals

$$E_A{}^U = \sum_{\mu(A)} P_{\mu\mu} U_{\mu\mu} \tag{3}$$

$$E_A{}^J = 0.5g_{ss}P_{ss}{}^2 + 0.5g_{pp}T_1 + g_{sp}T_2 + g_{pp'}T_3 + 2h_{sp}T_4 + 2h_{pp'}T_5 \tag{4}$$

$$E_A{}^K = -0.5g_{ss}P_{ss}{}^2 - 0.25g_{pp}T_1 - 0.5g_{sp}T_4 - 0.5g_{pp'}T_5 - 0.5h_{sp}(T_2 + T_4) - 0.5h_{pp'}(T_3 + T_5) \tag{5}$$

where:

$$T_1 = P_{xx}{}^2 + P_{yy}{}^2 + P_{zz}{}^2 \tag{6}$$

$$T_2 = P_{ss}(P_{xx} + P_{yy} + P_{zz}) \tag{7}$$

$$T_3 = P_{xx}P_{yy} + P_{xx}P_{zz} + P_{yy}P_{zz} \tag{8}$$

$$T_4 = P_{sx}{}^2 + P_{sy}{}^2 + P_{sz}{}^2 \tag{9}$$

$$T_5 = P_{xy}{}^2 + P_{xz}{}^2 + P_{yz}{}^2 \tag{10}$$

The subscripts A,B denote atoms in the molecule, μ,ν the running index of the atomic orbitals in the LCAO–MO, and (s,x,y,z) the 4 AOs forming the basis set of the atom (excluding hydrogen), while $P_{\mu\nu}$ is the bond-order matrix element. $U_{\mu\mu}$ represents the one-electron AO energy (*K.E.* + *P.E.*) of the electron in orbital μ of atom A, $g_{\mu\nu}$ ($= \langle\mu\mu|\nu\nu\rangle$) represents the coulombic repulsion energy between two electrons in orbitals μ and ν on atom A, and $h_{\mu\nu}$ ($= \langle\mu\nu|\mu\nu\rangle$) is the one-center exchange energy. The total monocentric coulombic (J) and exchange (K) energies $E_A{}^J$ and $E_A{}^K$ are derived from the expression for the total electronic energy by expanding the MOs in terms of the component AO's on atom A.

Care should be taken not to confuse the coulombic (J) and exchange (K) interactions with the one-center coulombic ($g_{\mu\nu}$) and exchange ($h_{\mu\nu}$) integrals. The terminology for J and K comes from the basic MO formalism.

Expressions for $E_A{}^J$ and $E_A{}^K$ have not been previously derived from the INDO approximation; note the differences between them and the corresponding CNDO expressions ($E_A{}^J$) and ($E_A{}^K$).

$$(E_A{}^J) = 0.5g_{ss}\left(\sum_{\mu} P_{\mu\mu}\right)^2 \tag{11}$$

$$(E_A{}^K) = -0.25g_{ss}\sum_{\mu}\sum_{\nu} P_{\mu\nu}{}^2 \tag{12}$$

Here all the one-center electron repulsion terms have a common value (g_{ss}) and $h_{\mu\nu}$ vanishes.

(b) Bicentric Terms. Analogous expansion of the bicentric terms (E_{AB}) in the MINDO/2 formalism leads to the following expressions.

$$E_{AB} = E_{AB}{}^R + E_{AB}{}^V + E_{AB}{}^J + E_{AB}{}^K + E_{AB}{}^N \tag{13}$$

$$E_{AB}{}^R = 2\sum_{\mu(A)}\sum_{\nu(B)} P_{\mu\nu}\beta_{AB}(I_\mu + I_\nu)S_{\mu\nu} \tag{14}$$

$$E_{AB}{}^V = (-P_AZ_B - P_BZ_A)\gamma_{AB} \tag{15}$$

$$E_{AB}{}^J = P_AP_B\gamma_{AB} \tag{16}$$

$$E_{AB}{}^K = -0.5\gamma_{AB}\sum_{\mu(A)}\sum_{\nu(B)} P_{\mu\nu}{}^2 \tag{17}$$

$$E_{AB}{}^N = Z_AZ_B\left[\gamma_{AB} + \left(\frac{1}{R} - \gamma_{AB}\right)e^{-\alpha_{AB}R_{AB}}\right] \tag{18}$$

Here P_A is the total electron density on atom A and Z_A is the effective core charge. The derivation of the two-center expressions is straightforward, being similiar to that of Fischer, *et al.*,[7] for their reparametrized CNDO method. We have used the MINDO/2 expressions for the core resonance integrals and core re-

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pulsion. The former (eq 14) is given by the Mulliken–Wolfberg–Helmholz approximation[14] while the latter (eq 18) is given by the Dewar–Klopman expression.[15]

(c) **Discussion.** The INDO expressions for the one-center terms seem at first sight superior to the CNDO ones since they distinguish between all the one-center repulsion integrals $g_{\mu\nu}$ and $h_{\mu\nu}$. This intuition is supported by the calculations reported here which suggest that the terms mainly responsible for changes in activation energy along the series **1**, **4**, **5**, **6** are the one-center terms ΔE_A. Previous work had suggested that while INDO is superior to CNDO for open shell systems[16] and in the study of magnetic properties,[17] both are comparable in their treatment of closed shell molecules.[18]

The dissection of the total energy into one-center and two-center terms conforms of course to the usual picture of molecules as composed of atoms linked by chemical bonds. E_{AB} provides a good quantitative measure of bond strength, both from its sign and from its magnitude. A large negative value for E_{AB} implies strong bonding between atoms A and B while a positive value implies an antibonding interaction. The component energies E_{AB} are chemically significant quantities because their sum is a measure of the heat of formation of the molecule. This is one of the advantages of the CNDO and INDO approximations; any such dissection would be much less convincing in more comprehensive treatments where three- and four-center interactions are included.

The individual components E_A and E_{AB} can, as we have seen, be further subdivided into contributions by the various terms in the Hamiltonian. Since these correspond to the various kinetic and potential terms contributing to the total energy of the molecule, this dissection is again physically meaningful.

Energy partitioning thus seems to offer a very attractive bridge between SCF calculations and chemistry, potentially more effective than current treatments based on the use of such quantities as bond energies or electron populations. The original studies by Fischer and Kollmar[7] certainly support this expectation. Moreover such an analysis of the energies of the reactants and products in a chemical reaction should throw light on the nature of the activation process.

We have therefore applied this technique to a study of the Cope rearrangement, for four reasons.

First, this is a reaction of considerable topical interest, the rate of which moreover varies in a striking way with the structure of the reactant.

Secondly, MINDO/2 studies[10,11] have proved very successful in interpreting the changes in activation energy with structure.

Thirdly, the compounds in question contain virtually all types of carbon–carbon bonds formed by sp^3 and sp^2 carbon atoms in environments involving varying degrees of strain.

And fourthly, we were interested to see to what extent such an analysis would confirm earlier suggestions[10,11] concerning the reasons for the variation in rate of the Cope rearrangement with structure.

Results and Discussion

A. **Cope Rearrangement.** The activation energies of the Cope rearrangements of **1** *via* **2** and **3**,[10] and of the bullvalene series **4–6**,[11] have recently been calculated by the MINDO/2 method. In each case the geometries of the ground states and transition states were optimized by a procedure due to Dr. A. Brown, based on the SIMPLEX method.[19] These calculations reproduced the large decrease in activation energy on passing from **1** to **4**, and also the further decrease in the series **4** > **5** > **6** (Table I).

Table I. Calculated and Observed Activation Energies (ΔE) (kcal/mole)

Compound	**1** (*via* **2**)	**1** (*via* **3**)	**4**	**5**	**6**
ΔE(calcd)	22.9	29.3	11.2	6.5	3.6
ΔE(obsd)	35.5[a]	41.2[b]	11.8,[c] 12.8[d]	8.6[e]	*f*

[a] Quoted by H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967). [b] Estimated from the value for **1** using results for the boat–chair difference reported by W. von E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962). [c] M. Saunders, *Tetrahedron Lett.*, 1699 (1963). [d] A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965). [e] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967). [f] Rearrangement still rapid on the nmr time scale at −110°; see H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

Table II shows total contributions of the one-center terms (E_A) for carbon and hydrogen atoms, and of the two-center terms (E_{AB}) for neighboring (N) and nonneighboring (NN) pairs of atoms AB. Values are listed for **1**, **4**, **5**, and **6**, for the two transition states **2** and **3**, and for the transition states **8–10** for rearrangement of **4**, **5** and **6**.

Table II. Dissection of Energies into One-Center and Two-Center Terms

Compound	ΣE_A, eV		ΣE_{AB}, eV	
	H	C	N[a]	NN[b]
1	−105.555	−613.907	−217.230	9.154
2	−105.863	−613.961	−216.399	9.676
3	−105.659	−615.940	−213.696	9.027
4	−105.608	−1026.125	−323.356	14.866
5	−105.506	−922.856	−296.963	13.004
6	−84.168	−820.965	−257.483	10.738
8	−105.458	−1025.730	−323.619	15.068
9	−105.337	−922.780	−298.435	14.513
10	−84.042	−821.067	−259.254	12.642

[a] Neighboring pair interactions. [b] Nonneighbor interactions.

Table III shows a similar dissection for the calculated activation energies of the various rearrangements, these being found by difference between the values for ground state and transition state.

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Table III. Dissection of Activation Energies into One-Center and Two-Center Terms

Compound	ΔE_A, eV			ΔE_{AB}, eV		
	H	C	Total	N	NN	Total
1 (*via* **2**)	−0.308	−0.054	−0.362	0.831	0.522	1.353
1 (*via* **3**)	−0.104	−2.033	−2.137	3.534	−0.127	3.407
4	0.150	0.395	0.545	−0.263	0.202	−0.061
5	0.169	0.076	0.248	−1.472	1.509	0.037
6	0.126	−0.102	0.024	−1.771	1.904	0.133

Table IV. Two-Center Terms for Rearrangements of **1** and **4**

Compound	E_{AB}, eV, and (in parentheses) R_{AB} bond length, Ångströms, for bond						
	a	b	c	d	e	f	g
				A			
1	−14.555 (1.510)	−15.216 (1.480)	−23.840 (1.321)	0.007 (3.903)	0.017 (3.394)		
2	−10.607 (1.596)	−17.736 (1.429)	−17.736 (1.429)	−10.607 (1.596)	−0.545 (2.570)		
3	−10.006 (1.630)	−17.695 (1.428)	−17.695 (1.428)	−10.006 (1.630)	−0.153 (2.630)		
4	−12.593 (1.506)	−15.638 (1.466)	−22.867 (1.337)	0.145 (2.428)	0.053 (3.043)	−12.593 (1.506)	−14.608 (1.487)
8	−8.182 (1.626)	−18.625 (1.408)	−18.625 (1.408)	−8.182 (1.626)	−0.062 (2.808)	−13.033 (1.489)	−13.033 (1.489)
				B: ΔE_{AB}			
3–1	4.549	−2.479	6.145	−9.999	−0.170		
8–4	4.411	−2.987	4.242	−8.327	−0.114	−0.440	+1.575
3–2	0.601	0.041	0.401	0.601	0.392		

The transition states **8–10** are derivatives of the "boat" transition state **3**. It will be seen that the greater facility of rearrangement in **4–6**, compared with that of **1** *via* **3**, is due to a large decrease in the terms $\Delta E_{AB}(N)$. This of course agrees with current intuition which attributes the ease of rearrangement in the bullvalene series to relief of ring strain. In passing from the ground state to the transition state, one bond in the old three-membered ring increases in length, while the new three-membered ring is not yet formed. If our correlation of two-center terms with corresponding bond energies is valid, we would expect the difference in activation energy to exhibit itself primarily in the terms $E_{AB}(N)$, and mainly in those for the σ bonds involved in the strained rings.

Table IV shows a detailed comparison of the relevant two-center CC interactions and calculated bond lengths in **1**, **2**, **3**, **4**, and **8**. Here and subsequently we will use the numbering of atoms and lettering of bonds indicated in Figure 1.

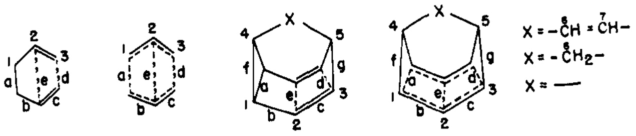


Figure 1. Numbering of atoms and lettering of bonds used in this paper; insert shows numbering of bridge atoms in bullvalene and barbaralene

The results in Table IV imply that the situation is more complicated than simple intuition would suggest. While it is true that the bonds in the cyclopropane ring of **4** seem to be weak judging by their E_{AB} values (*cf.* **4**a, f, g with **1**a, **1**b, or **4**b), the net change in the corresponding interactions in **4** (a, d, f, g) on passing to the transition state (−1.708 eV) is much *less* than the corresponding net change in **1**a and **1**d (−5.450 eV). On this basis, the ease of rearrangement of **4** cannot be attributed simply to relief of ring strain. Indeed, the main factor favoring **4** over **1** is rather the strength of the bonds (b, c) in the allylic moieties; the difference in net two-center interaction energy between these bonds in **8** and **4** (2.51 eV) is much less than that between **3** and **1** (7.132 eV). This difference is also reflected by the fact that the corresponding bonds are shorter (1.408 Å) in **8** than in **3** (1.428 Å), the former value being close to the average length (1.40 Å) for bonds in aromatic hydrocarbons. On this basis, the greater ease of formation of **8** is to be attributed not to ring strain as such but rather to increased stabilization of the delocalized bonds in the transition state.

However in this case one has to explain why the bonds in the allylic moieties of **8** should be stronger than those in **3**. Undoubtedly the answer is that the interactions between the allylic moieties are less in **8** than in **3** (*cf.* the E_{AB} values for bonds a and d) and this in turn probably reflects the effect of strain in the two terminal three-membered rings. In other words the greater reactivity of **4** is primarily due to ring strain, but this is obscured by a secondary redistribution of bond lengths with corresponding changes in the two-center energies.

The results in Tables III and IV also allow us to draw conclusions concerning the factors that favor **2** over **3**. It will be seen from Table III that there is a large difference in the one-center terms for carbon favoring **3**, but that this is outweighed by an even larger opposing difference in the two-center terms. Table IV shows that the latter difference is due to a greater loss of energy in bonds a and d on passing to the transition state, reflected by their greater length (chair, 1.596 Å; boat, 1.630 Å), and by a change of +0.392 eV in the interaction (e) between the central atoms of the allyl moieties. This is in good agreement

Table V. Two-Center Terms for **4–6** and **8–10**

Compound	E_{AB}(N), eV, and (in parentheses) R_{AB} bond length, Angströms, for bond a	b	c	d	e	f	g
				A			
4	−12.593	−15.638	−22.867	0.145	0.052	−12.593	−14.608
	(1.506)	(1.466)	(1.337)	(2.428)	(3.043)	(1.506)	(1.487)
5	−11.794	−16.070	−22.080	−1.268	0.038	−12.977	−14.395
	(1.549)	(1.456)	(1.352)	(2.063)	(3.019)	(1.492)	(1.473)
6	−10.536	−16.462	−21.907	−2.198	0.172	−13.100	−13.766
	(1.593)	(1.477)	(1.346)	(1.929)	(2.724)	(1.487)	(1.506)
8	−8.182	−18.625	−18.625	−8.182	−0.062	−13.033	−13.033
	(1.626)	(1.408)	(1.408)	(1.626)	(2.808)	(1.489)	(1.489)
9	−6.355	−18.979	−18.979	−6.355	0.141	−13.544	−13.544
	(1.720)	(1.405)	(1.405)	(1.720)	(2.680)	(1.488)	(1.488)
10	−5.910	−19.066	−19.066	−5.910	0.096	−13.458	−13.458
	(1.752)	(1.404)	(1.404)	(1.752)	(2.806)	(1.485)	(1.485)
				B: ΔE_{AB} (ΔR_{AB})			
8–4	4.411	−2.987	4.242	−8.327	−0.114	−0.440	1.575
	(+0.120)	(−0.058)	(+0.071)	(−0.802)	(−0.235)	(−0.017)	(+0.002)
9–5	5.239	−2.909	3.101	−5.087	0.103	−0.567	1.149
	(+0.171)	(−0.051)	(+0.053)	(−0.343)	(−0.339)	(−0.004)	(+0.015)
10–6	4.626	−4.604	2.841	−3.712	−0.066	−0.358	0.308
	(+0.159)	(−0.043)	(+0.058)	(−0.177)	(+0.082)	(−0.002)	(−0.021)

with the conclusions of simple perturbation theory[20] according to which the relative instability of **3** is due to an unfavorable orbital interaction between those atoms; the repulsion is tempered by stretching of the bonds (a, d) linking the allyl moieties and by an angular distortion which increases the e separation. The repulsive effects are thus distributed over bonds a and d as well as e.

Let us now consider the bullvalene series, **4–6**. Table III shows that their rearrangements differ in a remarkable way from that of **1**.

While the activation energy of **1** is due entirely to a decrease in total bond energy, as reflected in the two-center terms E_{AB}(N), and while the difference between the two isomeric transition states **2** and **3** is due to a change in the two-center terms, two-center terms apparently play only a minor role in the rearrangements of **4–6**. The net value of the contributions ΔE_{AB} is small and changes little along the series, and what change there is is opposite in direction to the overall change in activation energy. This of course can be attributed to the effect of ring strain which is probably much the same for all three compounds; the decrease in ring strain on passing from the reactants to the transition state just about balances the corresponding decrease in bond energy.

Table V shows the contributions of various bonds in **4–6**, and in the corresponding transition states **8–10**, to the total two-center interaction energy.

It will be seen that although the total sum of terms E_{AB} is small for all three compounds, the contributions of individual bonds are large and show large fluctuations along the series. Small changes in geometry evidently affect greatly the way in which the total energy is partitioned between different bonds. This, however, has little effect on the total energy, for since the geometry is such as to minimize the total energy, small changes in geometry have no first-order effect on that total.

Table VI. Dissection of One-Center Contributions to the Activation Energy for Rearrangement of **4**, **5**, and **6**

Compound	Carbon atom	$\Delta E_A{}^U$	$\Delta E_A{}^J$	$\Delta E_A{}^K$	ΔE_A(Tot)	$10^4\Delta q_A{}^a$
4	1	0.885	−1.180	0.192	−0.105	−266
	2	−3.205	3.504	−0.728	−0.429	772
	3	3.799	−3.707	0.645	0.736	−849
	4	−0.355	0.489	−0.061	+0.072	111
	5	−3.096	3.419	−0.724	−0.400	775
	6	−0.186	0.283	−0.019	0.078	64
	7	0.374	−0.226	0.090	0.238	−51
	Total[b]	−0.305	1.196	−0.496	0.395	
5	1	−1.176	0.959	−0.242	−0.459	215
	2	−1.294	1.461	−0.293	−0.126	322
	3	1.102	−0.968	0.126	0.260	−227
	4	1.741	−1.704	0.389	0.427	−384
	5	−1.099	1.256	−0.277	−0.120	+282
	6	1.350	−1.202	0.272	0.421	−275
	Total[b]	−0.744	1.254	−0.434	0.076	
6	1	−1.371	1.199	−0.296	−0.469	268
	2	−0.320	0.296	−0.077	−0.102	66
	3	−0.043	0.294	−0.086	0.165	60
	4	2.332	−2.339	0.483	0.476	−531
	5	0.494	−0.321	0.061	0.235	−77
	Total[b]	−0.643	0.917	−0.376	−0.102	

[a] Difference in total electron population in passing from ground state to transition state, *i.e.*, $\Delta q_A > 0$ implies a gain in density density, *i.e.*, the formal charge becomes more negative. [b] Summed up over all carbon atoms in the molecule.

The main contribution (Table III) to the activation energies of **4–6** comes then from changes (ΔE_A) in the one-center terms E_A on passing from reactant to transition state; moreover the contribution of hydrogen atoms is almost constant along the series, the change in activation energy being due to changes in the one-center terms for carbon. These are listed in Table VI. Table VI also shows a breakdown of the terms ΔE_A into their components $\Delta E_A{}^U$, $\Delta E_A{}^J$, and $\Delta E_A{}^K$ (eq 3–5). It will be seen that while $\Delta E_A{}^U$ and $\Delta E_A{}^J$ are both large, they almost cancel one another, the values ΔE_A for the individual carbon atoms parallelling quite closely those for $\Delta E_A{}^K$. The last column of Table VI shows the change (Δq_A) in the electron population of atom A in passing from the reactant to the transition state; *i.e.*, Δq_A positive implies an increase in electron density and so in negative charge. It will be seen that the changes in ΔE_A and $\Delta E_A{}^K$ are correlated with those

(20) M. J. S. Dewar, *Angew. Chem.*, in press.

in Δq_A, an increase in electron density making ΔE_A and ΔE_A^K more negative. This can be understood quite easily in general terms. When q_A increases, the total one-center core binding energy increases so E_A^U becomes more negative, while the one-center coulombic repulsion E_A^J increases. Since both terms vary with q and in opposite directions, the net effect is mainly due to the "nonclassical" exchange term ΔE_A^K. However although this trend holds for most of the individual carbon atoms in the various compounds of the series, the differences in total monocentric energy ($4 > 5 > 6$; Table VI) are still determined primarily by changes in the total coulomb term ΔE_A^J.

The changes in Δq_A, and hence in ΔE_A, can in turn be related to changes in geometry along the series. The most abrupt change is in the length of bond d, Table V. In passing from **4** to **8**, this decreases by 0.802 Å; in passing from **5** to **9** by 0.343 Å; and in passing from **6** to **10** by only 0.177 Å. The decrease in length of bond d should tend to force electrons of the terminal atoms (3) on to neighboring atoms (2, 5); this effect is shown very clearly by the corresponding terms Δq_A in Table VI.

It will be seen that the terms leading to decreasing activation energy along the series **4**, **5**, **6** are those for the carbon atoms in the "aromatic ring" of the transition state, *i.e.*, atoms 1, 2, and 3. Moreover this trend is accompanied by a marked reversal of charge transfer between these positions and the rest of the carbon skeleton. In bullvalene (**4**), the net electron population on the six "aromatic" atoms decreases by 0.686 on passing to the transition state while that on the remaining atoms increases by 0.899. In barbaralane (**5**) the situation is reversed, the aromatic electron population *increasing* by 0.620 and the nonaromatic population *decreasing* by 0.377. In semibullvalene (**6**) the aromatic population increases still more (by 0.788) while that of the nonaromatic atoms decreases by 0.608.

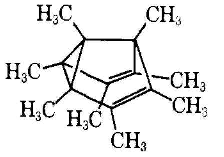
Examination of the ΔE_{AB} values and bond lengths in Table V shows that the bonds linking the allyl moieties (a and d) in the transition states increase in length in the order $\mathbf{8} < \mathbf{9} < \mathbf{10}$, while the bonds in the allyl moieties (b and c) contract in the same order. The implied decrease in (a + d) bonding is reflected by the changes in the sum of the corresponding two-center terms ($\Delta E_a + \Delta E_d$) along the series (−3.916, +0.154, +0.194) and the implied increase in (b + c) bonding by corresponding changes in the sum ($\Delta E_b + \Delta E_c$) (+ 1.255, +0.122, −1.763).

Evidently the transition state becomes increasingly like a pair of allyl radicals as the length of the bridge X (Figure 1) is decreased. The six carbon atoms involved apparently become effectively more electronegative, and the transition state is correspondingly stabilized by a drift of charge to them from the rest of the molecule.

This of course leads to interesting deductions concerning the effects of substituents. Substituents which increase the electronegativity of the "aromatic" carbon atoms should tend to stabilize the transition state and so facilitate reaction, particularly in the case of **6**, while electron-releasing substituents should have the opposite effect.

There are no data as yet to test this prediction. However it is interesting that the activation energy for rearrangement of dihydrobullvalene (9.5 kcal/mol[21]) is considerably less than that (11.8[22] or 12.8[23] kcal/mole) of bullvalene; since sp^2 carbon is more electronegative than sp^3 carbon, the bridge in the dihydro derivative should be a better electron source. Conversely, replacement of the methylene bridge in barbaralane by the more electron-attracting carbonyl raises the activation energy from 8.6[24] to 9.6[25] kcal/mole. Recently Anet and Schenck,[26] have measured the activation energy for octamethylsemibullvalene; since their value (6.4 kcal/mole) is considerably greater than that (3.3 kcal/mole) calculated for semibullvalene itself, this may reflect the effect of electron-releasing substituents (*i.e.*, methyl) in the allyl moieties.

Our calculations suggest that electron-withdrawing groups, particularly in the 1 and 3 positions, should lower the activation energy; since this is already so small, substituents of this type could well stabilize the "transition state" to a point where it became the stable species. A good objective in this connection would be compounds **12** where X could be CF_3, CN, COOH, etc., or the aza analog **13**.



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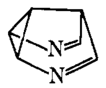

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Another interesting possibility might be the converse stabilization of the barbaralane intermediate **9** by introduction of electron-releasing groups into the nonaromatic section, or replacement of carbon atoms by heteroatoms. We are studying the effects of such structural changes by detailed MINDO/2 calculation.

One final point: it will be seen that the calculations and arguments reported here imply that interactions between the central atoms of the allyl moieties in the Cope transition state (*i.e.*, e in Figure 1) play only a minor role in determining the rate of rearrangement. While these interactions do seem to account for the preferred adoption of "chair-type" transition states in the rearrangement of acyclic 1,5-hexadienes, they do not seem to play any significant part in determining the relative rates of rearrangement of the various bullvalene-type compounds. This conclusion conflicts with that reached by Simonetta, *et al.*,[12] from an analogous analysis of their CNDO/2 calculations for the rearrangement of **7** where they found comparable values for the two-center terms corresponding in the notation of Figure 1 to bonds a, d, and e. They concluded that the transition state involves three-center interactions between the allyl moieties. The reason for this difference is easily seen; in their calculated geometry, bonds a, d, and e are comparable in length, whereas in the transition states considered here, e is much longer than a or d. It is possible that this

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distinction is real and a consequence of the peculiar geometry of **7**; however we suspect that it may have been an artifact of the simplifying assumptions made by Simonetta, *et al.*, in order to reduce the amount of computation and that a rigorous minimization of the energy of the transition state would lead to conclusions similar to those presented here.

B. Origin of Chemical Bonding. We have assumed in the previous discussion that the two-center terms E_{AB} are measures of chemical bonding; it is, however, by no means self-evident that any exact correlation should exist between the bond energies of classical theory and the corresponding terms E_{AB} because the heat of formation is by no means equal to a sum of the terms $E_{AB}(N)$ for neighboring pairs of atoms. There are large contributions from the one-center terms E_A, corresponding to differences between atoms in isolation and atoms in molecules, and also of course from terms $E_{AB}(NN)$ for nonneighbor interactions.

One can see from the results listed above that there is at least a qualitative correspondence between E_{AB} and bond strength; thus the values of E_{AB} for the double bonds are very large while those for the bonds in cyclopropane rings are less than those for "unstrained" single bonds. Equally one can see that there is no direct equality between the two quantities because the values for E_{AB} are far larger than the corresponding bond energies; thus for C–C and C=C bonds, the values of E_{AB} are *ca.* 15 eV (350 kcal/mole) and 22 eV (505 kcal/mole), respectively, roughly four times the corresponding bond energies or bond strengths.

Figure 2 shows a plot of the E_{AB} values for CC bonds in compounds considered in this paper *vs.* their calculated bond lengths. It will be seen that the points all lie close to a single curve, this being true both for bonds in the parent molecules **1**, **4**, **5**, and **6**, and for those in the transition states **2**, **3**, **8**, **9**, and **10**. The relation is not linear; this, however, is not at all surprising given that the E_{AB} values are so much greater than the corresponding bond energies. It is indeed rather surprising that bond length should be so closely determined by E_{AB}, given that three-quarters of the bicentric contributions are apparently cancelled by other terms.

Equations 13–18 provide a basis for dissecting the bicentric contributions E_{AB} into components E_{AB}^R, E_{AB}^V, E_{AB}^J, E_{AB}^K, and E_{AB}^N. When this is done, a remarkable regularity appears. Although E_{AB}^V, E_{AB}^J, and E_{AB}^N are larger by an order of magnitude than the two remaining terms, it seems to be the term E_{AB}^R, representing the contribution of one-electron resonance integrals, that determines the effective bond energy. The contribution of the other terms cancels to a remarkable approximation. While approximate cancellation might have been expected on the grounds that overall coulomb forces between atoms in neutral molecules should be small, one could not have anticipated that the compensation would be so effective. The relative magnitude of the various terms is indicated by typical examples in Table VII, while Figure 2 also shows a plot of bond length *vs.* E_{AB}^R. It will be seen that the relation between the two is as good as that between bond length and E_{AB} and also that the values for E_{AB}^R are very similar to those for E_{AB}, being less by 5–10%.

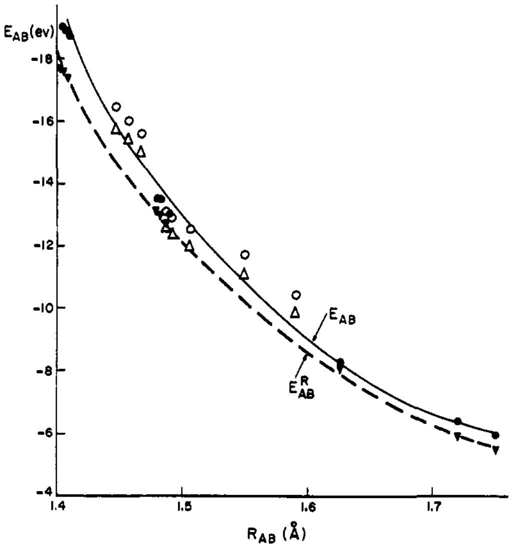

Figure 2. A plot of E_{AB} against R_{AB}: ○GS, ●TS (———) and E_{AB}^R against R_{AB}: △GS, ▼TS (— — —) for bonds a, b, and f in molecules **4**, **5**, **6**, **8**, **9**, and **10**.

Table VII. Dissection of Average Values[a] of E_{AB} for Various Bonds into Components

Bond	E_{AB}^V	E_{AB}^J	E_{AB}^K	E_{AB}^N	E_{AB}^R	E_{AB} (total)
C–C	−236	118	−4	121	−15	−15
C=C	−246	123	−6	127	−19	−22
C–H	−68	34	−4	37	−11	−12

[a] Energies in eV.

Ruedenberg[27] some time ago gave convincing arguments for believing that the resonance terms E_{AB}^R should be the most important in determining the strengths of π bonds in conjugated systems; it is, however, difficult to tell on the basis of theoretical arguments to what extent the situation will be dominated by such terms. The analysis given here certainly suggests that the resonance terms also predominate in σ bonds; this presumably accounts for the qualitative success of treatments of Hückel type where other factors are to a large extent neglected. At the same time, as Figure 2 shows, the correspondence is not complete. Although the points there do lie close to a single curve, there is quite a lot of scatter, the deviations being in fact large in a chemical sense (where 1 eV is a huge amount of energy!). It is therefore also far from surprising that Hückel-type treatments should prove unreliable in a quantitative sense.

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