Studies of Reaction Mechanisms by All-valence Electron Semi-Empirical SCF MO Theories. VIII.[1] Electronic Structure and Valence Isomerization of *syn*- and *anti*-Tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes

Hiizu Iwamura, Hiroshi Kihara, Kazuhiko Morio, and Tosiyasu L. Kunii*
*Department of Chemistry, Faculty of Science, *Information Science Laboratory, Faculty of Science, and The Computer Centre, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

(Received April 5, 1973)

The theoretical structures and heats of formation of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (**1** and **2**) have been investigated by the MINDO methods. An examination of their MO's reveals that there is an extensive mixing between the highlying σ-orbitals of the four-membered rings and the ethylenic π-orbitals, which makes the highest occupied MO's devoid of any ethylenic π-character. A degenerate valence isomerization (Eq. (7)) rather than the [2+2] cycloaddition is suggested as an excited-state reaction. An intermediately facile ($\Delta H^{\neq}=23.1$ kcal/mol) degenerate Cope rearrangement (Eq. (1)) is predicted for **1** under thermal conditions. The transition-state structure (**1′**) and the partitioned activation energy values obtained by the MINDO/2 methods are compared with those for the Cope rearrangement of semibullvalene (**3**) and 1,5-hexadiene. The deviation from planarity of the allyl groups in **1′** is the reason for the activation energy calculated for **1** being higher than that for **3**. The hypothetical paths from **1** to cubane in the electronic ground state are characteristic of the reaction with an anti-aromatic transition state.

Although the development of the chemistry of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (**1** and **2**) has been rather tardy since their first preparation as cyclobutadiene dimers by Nenitzescu and his co-workers in 1964,[2] their electronic structures are of great theoretical interest in that extensive through-space and/or through-bond interaction[3] between π- and high-lying σ-orbitals is expected. We will present here some possible chemical consequences of the orbital overlap as revealed by an examination of their molecular orbitals obtained by the MINDO approximations which are reputed to reproduce the ground-state properties of hydrocarbons reasonably well.[4] Two kinds of the valence isomerization of the *syn*-isomer **1**, one involving a degenerate Cope rearrangement and the other leading to cubane (Chart 1), are considered.

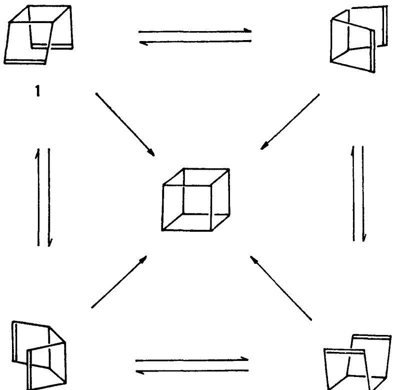
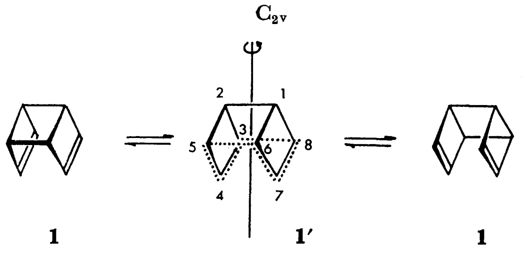


Chart 1

Method of Calculations

Since no structural data are available for **1** and **2**, their equilibrium geometries are sought by minimizing the total energies with respect to the changes in all the independent bond lengths and angles in the molecules. The geometry of the transition state **1′** for the Cope rearrangement was assumed *a priori* to have the C_{2v} symmetry, with the axis passing through the centers of the C_1–C_2 and C_4–C_7 bonds when the C_5–C_6 and C_3–C_8 bonds participate in the rearrangement (Eq. (1)); it was optimized much as in ground-state geometry.



(1)

1 **1′** **1**

In order to help verbalize the results of the molecular orbital studies, the partitioning of the total energy into one-center and two-center terms was carried out as presented by Gordon[5] and by Fischer and Kollmar[6] for the CNDO methods. In the framework of the MINDO/2 methods, both terms are defined by standard integrals as follows, with the second term consisting of the resonance (E_{AB}^{R}), exchange (E_{AB}^{X}), and electrostatic (E_{AB}^{S}) terms, respectively:

$$E_{\text{total}} = \sum_{A} E_{A} + \sum\sum_{A<B} E_{AB} \tag{2}$$

$$\begin{aligned} E_{A} = {} & \sum_{\mu(A)} P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu(A)} P_{\mu\mu}^{2} \langle \mu\mu | \nu\nu \rangle \\ & + \sum_{\mu\neq\nu}^{A} \sum^{A} \Big\{ P_{\mu\mu} P_{\nu\nu} \Big[\langle \mu\mu | \nu\nu \rangle - \frac{1}{2} \langle \mu\nu | \mu\nu \rangle \Big] \\ & + P_{\mu\nu}^{2} \Big[\frac{3}{2} \langle \mu\nu | \mu\nu \rangle - \frac{1}{2} \langle \mu\mu | \nu\nu \rangle \Big] \Big\} \end{aligned} \tag{3}$$

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1) Part VII: H. Iwamura, K. Morio, and H. Kihara, *Chem. Lett.*, **1973**, 457.

2) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

3) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

4) a) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969); b) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

5) M. S. Gordon, *ibid.*, **91**, 3122 (1969).

6) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

$$
\begin{aligned}
E_{\mathrm{AB}} &= E_{\mathrm{AB}}^{\mathrm{R}} + E_{\mathrm{AB}}^{\mathrm{X}} + E_{\mathrm{AB}}^{\mathrm{S}} \\
E_{\mathrm{AB}}^{\mathrm{R}} &= 2\sum_{\mu(\mathrm{A})}\sum_{\nu(\mathrm{B})} P_{\mu\nu}\beta_{\mathrm{AB}}(I_\mu+I_\nu)S_{\mu\nu} \\
E_{\mathrm{AB}}^{\mathrm{X}} &= -\frac{1}{2}\gamma_{\mathrm{AB}}\sum_{\mu(\mathrm{A})}\sum_{\nu(\mathrm{B})} P_{\mu\nu}^2 \\
E_{\mathrm{AB}}^{\mathrm{S}} &= P_{\mathrm{A}}P_{\mathrm{B}}\gamma_{\mathrm{AB}} + (-P_{\mathrm{A}}Z_{\mathrm{B}}-P_{\mathrm{B}}Z_{\mathrm{A}})\gamma_{\mathrm{AB}} \\
&\quad + Z_{\mathrm{A}}Z_{\mathrm{B}}[\gamma_{\mathrm{AB}}+(1/R-\gamma_{\mathrm{AB}})\exp(-\alpha_{\mathrm{AB}}R_{\mathrm{AB}})]
\end{aligned} \tag{4}
$$

In short, the total energy of molecules is considered to be determined by the nature of the constituent atoms and the chemical bonding energy, E_{AB} corresponding to the strength of the A–B bond. By taking a partial summation, the one-center energy is further divided into one due to hydrogen and another due to carbon atoms:

$$\sum_{\mathrm{A}} E_{\mathrm{A}} = \sum E_{\mathrm{A}}{}^{\mathrm{H}} + \sum E_{\mathrm{A}}{}^{\mathrm{C}} \tag{5}$$

The two-center terms are further subdivided to neighboring ($E_{\mathrm{AB}}^{\mathrm{N}}$) and non-neighboring ($E_{\mathrm{AB}}^{\mathrm{NN}}$) terms, where the A and B atoms in $E_{\mathrm{AB}}^{\mathrm{N}}$ are, by definition, a pair connected by the chemical bond, while the pair of A and B in $E_{\mathrm{AB}}^{\mathrm{NN}}$ are not directly bonded in a molecule.

The calculations were performed on a HITAC 5020E computer, with the use of a modified MINDO program originally written by Baird and distributed by the QCPE organization.[7]

Results and Discussion

(A) Results on Ground-state Geometry and Energy. The equilibrium geometries, neighboring two-center energies, and bond indices of Wiberg, as defined as Eq. (6),[8] are summarized for **1** and **2** in Table 1.

$$W_{\mathrm{AB}} = \sum_{\mu}^{\mathrm{A}}\sum_{\nu}^{\mathrm{B}} P_{\mu\nu}^2 \tag{6}$$

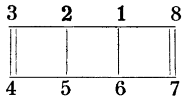
The calculated bond lengths and angles are generally in good agreement with those observed for many cyclobutane and cyclobutene derivatives,[9] especially when the slight underestimation of the sp^2 to sp^3 single-bond length is taken as a natural consequence of one of the disadvantages of the MINDO/2 approximations.

The heats of formation and the ionization potentials obtained by the use of Koopmans' theorem are listed in Table 2. The MINDO/1 energy values are for the geometries of **1** and **2**, which are obtained by replacing the optimized bond lengths by the MINDO/2 with the standard bond lengths tabulated in Ref. 4(a). It is generally accepted that the strain energy of cyclobutane and cyclobutene rings is underestimated by the MINDO/2 by as much as 25 kcal/mol.[4] The values of the heat of formation calculated for **1** and **2** by this method are lower than those of the MINDO/1 by *ca.* 75 kcal/mol. The value when divided by three, the number of the four-membered rings present in **1** and **2**, gives 25 kcal/mol, in good agreement with the amount of the underestimation of the strain energy per four-membered ring. Thus, the MINDO/1 values are considered to represent more realistic theoretical values for the heat of formation. The value of 108 kcal/mol is obtained for **1** and **2** by Franklin's group-equivalent method for the heat of formation.[10]

The ionization potentials calculated by the MINDO/2 are in good agreement with the experimental ones.[11] The larger value found for **2** is well reproduced by the calculation; the origin of the difference in **1** and **2** will be discussed in Section (B).

We note that the **1** isomer is always predicted to be slightly less stable than the **2** isomer irrespective of the approximation of the MO methods employed. The **1**

TABLE 1. GROUND STATE GEOMETRIES, TWO-CENTER ENERGY TERMS, AND WIBERG'S BOND INDICES OF TRICYCLO[4.2.0.0^{2,5}]OCTA-3,7-DIENES **1** AND **2**



		C_1C_2	C_2C_3	C_3C_4	C_1C_6	C_3C_8	Cyclobutane-cyclobutene dihedral angle
1	Bond length (Å)	1.50	1.48	1.33	1.55	2.93	119°
	$E_{\mathrm{AB}}^{\mathrm{N}}$ (eV)	−13.577	−14.435	−22.748	−12.468	0.060	
	Wiberg's bond index	0.934	0.979	1.903	0.965	0.0024	
2	Bond length (Å)	1.505	1.48	1.33	1.55	3.85	116°
	$E_{\mathrm{AB}}^{\mathrm{N}}$ (eV)	−13.731	−14.467	−22.738	−12.432	−0.034	
	Wiberg's bond index	0.945	0.977	1.903	0.959	0.0084	

TABLE 2. DISSECTED TOTAL ENERGIES, HEATS OF FORMATION AND IONZIATION POTENTIALS OF TRICYCLO[4.2.0.0^{2,5}]OCTA-3,7-DIENES **1** AND **2**

	E(eV)		ΔH_f (kcal/mol)		Ionization potential (eV)		
	$\sum E_{\mathrm{A}}$	$\sum\sum E_{\mathrm{AB}}$	MINDO/1	MINDO/2	MINDO/1	MINDO/2	Observed[11]
1	−906.064	−245.275	120.8	46.3	9.38	8.86	8.20
2	−906.064	−245.424	120.2	42.9	9.25	9.07	8.27

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[7] Quantum Chemistry Program Exchange No. 137, Chemistry Department, Indiana University, Bloomington, Indiana 47401.

[8] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[9] S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **92**, 5250 (1970), and the papers cited therein.

[10] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[11] J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.*, **91**, 5940 (1969).

TABLE 3. NON-NEIGHBORING TWO CENTER ENERGIES E_{AB}^{NN} (eV) FOR **1** AND **2**

	AB	E_{AB}^{R}	E_{AB}^{X}	E_{AB}^{S}	E_{AB}^{NN}
1	C_3C_8	0.024	−0.006	0.042	0.060
	C_3H_9	−0.033	−0.010	0.009	−0.034
	H_9H_{10}	0.001	−0.000	0.074	0.074
2	C_3C_8	−0.023	−0.015	0.004	−0.034
	C_3H_9	0.025	−0.003	0.047	0.070
	H_9H_{10}	−0.054	−0.007	0.032	−0.030

isomer is calculated by the CNDO/2 method as well to be less stable by 2.4 kcal/mol. It is intuitively expected that the repulsive interaction between the 2pπ orbitals of the two facing ethylene groups in **1** might contribute to the destabilization, since the distance between the ethylene groups is only 2.93 Å. The energy partitioning study supports this expectation. The non-neighboring two-center energy value for C_3 and C_8 (=C_4 and C_7) is *ca.* 1.5 kcal/mol; the positive sign indicates destabilization, and the mechanism is found to be mostly electrostatic (see Table 3).[12] The slight widening of the angles between the cyclobutane and cyclobutene ring planes calculated for **1** compared to **2** could be due to this repulsive interaction. A further inspection of the dissected energy values reveals that, although the eclipsed hydrogen atoms, H_9 and H_{10}, in **1** also have non-neighboring repulsion, the effect is counterbalanced by the analogous interaction between pairs of eclipsed hydrogen and carbon atoms on the cyclobutane ring in **2**. The bonding interaction between the far-apart C_3 and C_8 (and C_4 and C_7 as well), together with the strengthening of the C_1–C_2 bond (and C_5–C_6) in **2**, as is shown in Table 2, suggest the role of a through-bond resonance interaction, *i.e.*, π-σ-π conjugation, between the two ethylenic moieties as another factor favoring **2** energetically.

(B) Molecular Orbital Construction. Turning now to the construction of the higher occupied molecular orbitals of **1** and **2**, we may note that the π-orbital approximations are a far from satisfactory description. The highest occcupied molecular orbitals are, first of all, not π-charactered, but are composed of σ-orbitals. The mixing of the ethylenic π-orbitals with σ-orbitals is extensive as a result of the presence of the high-lying σ-orbitals of cyclobutane and cyclobutene rings.[13] The unique topology of the carbon atoms in **1** and **2** also provides the necessary symmetry for the interaction. Ideally, three types of interaction, a, b, and c, are possible between the 2p-orbitals, as is shown in Chart 2. In connection with the relative stability of **1** and **2** discussed in the previous section, the a type interaction

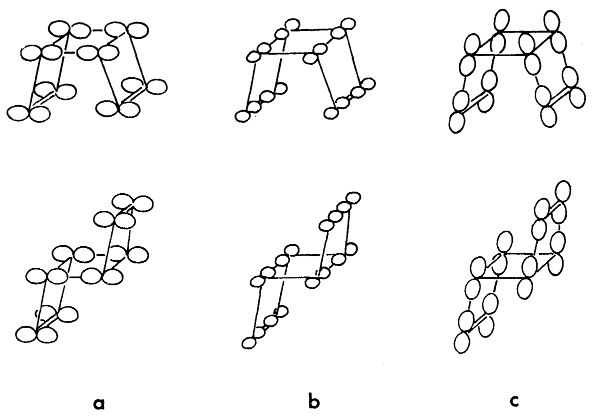

Chart 2

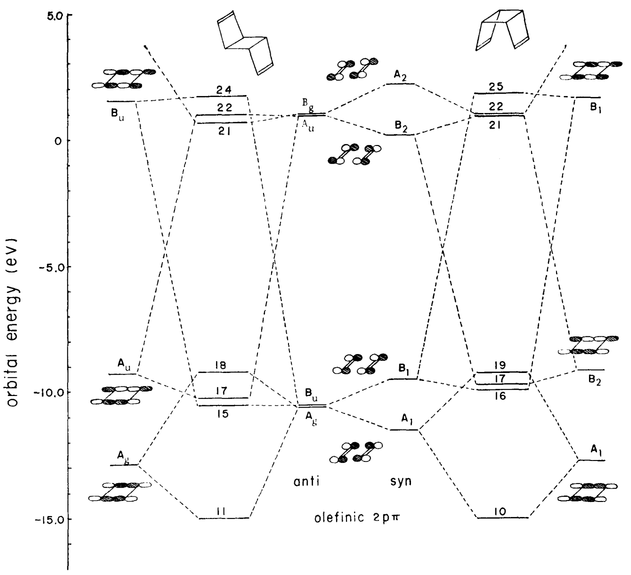

Fig. 1a. Type a interaction diagram for the mixing of two olefinic 2pπ orbitals and the σ orbitals of a cyclobutane ring. Symmetry classification uses the σ and i operations for **1** and **2**, respectively.

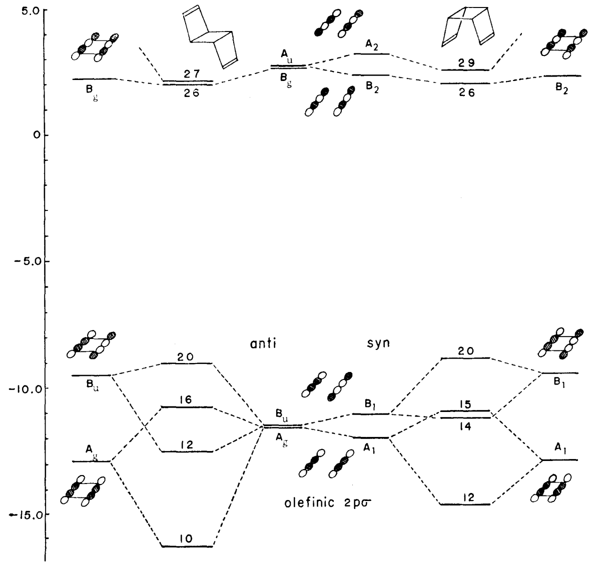

Fig. 1b. Type b interaction diagram for the mixing of two olefinic 2pπ orbitals and the σ orbitals of a cyclobutane ring. The directions of the atomic orbitals are idealized.

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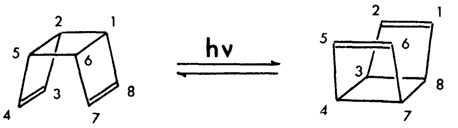
[12] The sum of the Hückel molecular orbital energy values should not change theoretically by the interaction of the two facing ethylene groups, because the amount of the stabilization of the in-phase combination of the ethylenic π-orbitals and the destabilization of the out-of-phase combination cancel each other out. The terms other than electrostatic are, therefore, expected not to differ much between **1** and **2**.

[13] L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969); R. Hoffmann and R. B. Davidson, *ibid.*, **93**, 5699 (1971); J. S. Wright and L. Salem, *ibid.*, **94**, 322 (1972); P. Bischof, E. Haselbach, and E. Heilbronner, *Angew. Chem.*, **82**, 952 (1970).

is of prime importance in that many of the calculated higher occupied molecular orbitals are interpreted in terms of this type of interaction. The calculated coefficients of the atomic orbitals in the 10th, 16th, 17th, and 19th molecular orbitals of **1**, for example, are described by interaction diagram of Fig. 1a. To this is added the b type interaction, which results in the production of the highest occupied 20th molecular orbital of a σ-character. It is interesting to note that the lower ionization potential calculated for **1** compared to **2**, *i.e.*, the energy value of the highest occupied molecular orbital of **1** relative to **2** higher by 0.21 eV, is due to a larger splitting by this interaction in **1**, probably because of the through-space destabilization of the ethylenic σ-bonds. The failure to obtain cubane by the irradiation of **1** under direct and sensitized conditions[14] is possibly related to the fact that the highest occupied molecular orbital is not connected with the ethylenic π-orbitals. To make matters worse, the C_1–C_6 and C_2–C_5 bonds of the cyclobutane ring are now *anti*-bonding in the unoccupied molecular orbitals, *e.g.*, 21st and 26th, where the transannular π-orbital interaction between C_3 and C_8, and between C_4 and C_7, is effectively bonding. Thus, the cleavage of the ring would concomitantly result and a degenerate valence isomerization as depicted by Eq. (7) can be predicted as a possibility of an excited-state reaction.[1]



(7)

(C) Results on the Transition State for the Cope Rearrangement. Figure 2 shows the optimized geometry and (in parentheses) the Wiberg bond indices for the transition-state structure **1′**. The four-membered rings are folded so as to make a dihedral angle between the $C_2C_3C_5$ and $C_3C_4C_5$ planes of 25.8°. Notice also that each allyl group is not planar, but that the end carbon atoms, C_3, C_5, C_6, and C_8 are pyramidal, with the hydrogen atoms attached to them deviating outwards from the trigonal planes, *e.g.*, the $C_2C_3C_4$ plane, by 32.0°. The geometry is considered to be attained by an attempt to relieve the non-bonded interaction between the facing hydrogens on both sides of the allyl moieties on the one hand and to increase the overlap between the two allyl groups at their ends. In contrast, the hydrogen atoms attached to C_4 and C_7 are displaced by 14.5° from the $C_3C_4C_5$ and $C_6C_7C_8$ planes, respectively, in the direction of their approach. The deformation is favored by the smaller overlap between C_4 and C_7. When the overlap is appreciable, the intermediate will be somewhat like the geometry on the reaction coordinate leading to cubane and should be energetically unfavorable, as will be seen in Section (E). The distance between the two allyl groups in **1′** is 1.71 Å at the end carbons and 2.70 Å at the center. These values are quite similar to the corresponding values (1.75 and 2.81 Å respectively)[15] in the transition-state structure for the Cope rearrangement of semibullvalene **3**. In other words, the delocalization of electrons over the six carbon atoms (C_3 through C_8) in **1′** is expected to be as extensive as in the transition state of **3**. The heat of formation of **1′** obtained by the MINDO/2 method is 69.5 kcal/mol.

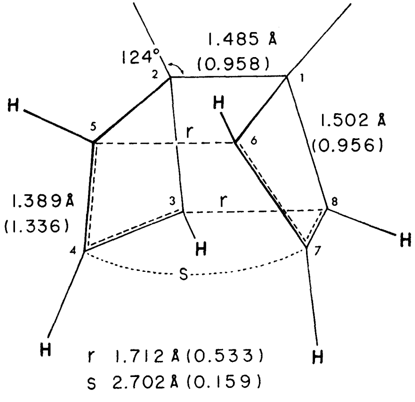


Fig. 2. The optimized bond lengths and the Wiberg's bond indices (in parentheses) for **1′**.

(D) On the Activation Energy for the Cope Rearrangement. The activation energy for the Cope rearrangement of **1** *via* **1′** is calculated as 23.1 kcal/mol on the basis of the difference between the MINDO/2 heats of formation for the ground state, **1**, and the transition state, **1′**.[16] Although the Cope rearrangement in **1** can be expected, from the similarity of the transition-state structure, to be as facile as in the case of **3** (see Section (C)), the value indicates that the reaction is not as easy as in bridged homotropilidenes, in which the activation energy is no more than 12 kcal/mol.[15] The reported thermal isomerizations of 1,3,4,6-tetrabromo-2,5,7,8-tetramethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene to the 1,4,5,8-tetrabromo-2,3,6,7-tetramethyl isomer (Eq. (8)) and of the hexachloro-derivative (Eq. (9)) support the result of the theoretical calculations.

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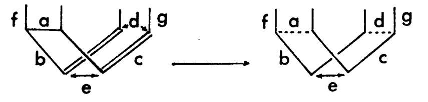
[14] R. Criegee, *ibid.*, **74**, 703 (1962); H. Iwamura, to be published elesewhere.

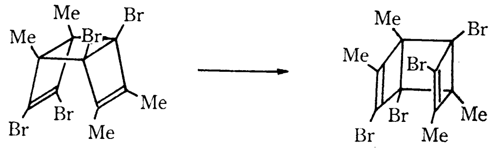
[15] A. Brown, M. J. S. Dewar, and W. W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970); M. J. S. Dewar and D. H. Lo, *ibid.*, **93**, 7201 (1971); H. Iwamura, K. Morio, and T. L. Kunii, This Bulletin, **45**, 841 (1972).

[16] A more reasonable energy value which includes the correct strain energy in **1′** may be obtained by the MINDO/1 calculation. There is, however, a fatal ambiguity in the latter method as regards the choice of the correct standard bond lengths for the allyl groups in **1′**. There are no *a priori* standard bond lengths tabulated for the bonds of an intermediate bond order or hybridization, and yet the calculated energy values are rather sensitive to these bond lengths. Although there is certainly strain energy in **1′** due to the presence of two four-membered rings, and although the release of the strain energy of one cyclobutane ring can be expected on going from **1** to **1′**, the effect is considered to be partly counterbalanced by the formation of two less strained cyclobutane-like rings approaching bicyclo[2.2.0]hexane in **1′**. Thus, as long as the difference in heats of formation is concerned, the MINDO/2 value is taken to represent a more reliable estimate of the activation energy for the degenerate Cope rearrangement of Eq. 1. Since the strain energy in **1** is still underestimated relative to that in **1′**, the activation energy obtained as heats of formation of the latter minus that of the former is likely to be overestimated. The value of 23.1 kcal/mol, may, therefore, be proposed as the upper limit of the activation energy.

Table 4. One-center and two-center terms in the activation energies for the Cope rearrangements of **1**, **3** and **4**

	ΔE_A (eV)		ΔE_{AB}(eV)		ΔE_{AB}(eV) and (in parentheses) bond length (Å) in the transition state for bonds						
	H	C	N	NN	a	b	c	d	e	f	g
1	−0.010	−1.051	1.967	0.097	5.968	−3.527	4.786	−7.669	−0.025	−0.934	1.033
					(1.712)	(1.389)			(2.702)		
3	0.126	−0.102	−1.771	1.904	4.626	−2.604	2.841	−3.712	−0.076	−0.358	0.308
					(1.752)	(1.404)			(2.806)		
4	−0.104	−2.033	3.534	−0.127	4.549	−2.479	6.145	−10.013	−0.170	—	—
					(1.630)	(1.428)			(2.630)		





(8)[17]

(9)

Table 4 shows the total contributions to the activation energy of the one-center term (ΔE_A) for the carbon and hydrogen atoms, and of the two-center terms (ΔE_{AB}) for the neighboring (N) and non-neighboring (NN) pairs of the AB atom. These values are compared with those of the Cope rearrangements of 1,5-hexadiene **4** *via* the boat-type transition state and of semibullvalene **3**. These examples represent two extreme cases with respect to the facility of the reaction; the activation energies are *ca.* 40 kcal/mol[18] for the former and less than a few kcal/mol for the latter.[19]

The one-center terms, ΔE_A, for **1** to **1′** are characterized by an intermediately large negative value for carbon atoms. The effect is pronounced for the carbon atoms, $C_5(C_6)$ (−0.343 eV) and $C_4(C_7)$ (−0.354), in the allyl groups. The negative values of $\Delta E_A{}^C$ are parallel with the change (Δq_A) in the electron population of carbon atoms in passing from the reactant to the transition state; the Δq_A's are 0.008, 0.019, and −0.034 for $C_5(C_6)$, $C_4(C_7)$, and $C_3(C_8)$ respectively. The correlation can be understood quite easily by taking into account the change in the electronegativity of the carbon atoms which undergo rehybridization. On passing to the transition state, the s character of the orbitals directed from carbon atoms C_5 and C_6 to the adjoining atoms is increased, while it is decreased at C_3 and C_8. The decrease in the electronegativity of the latter carbons should tend to force the electrons on these atoms on to the neighboring C_4 and C_7. The increase in the electron population leads to the increase in the total one-center core attraction energy, $\Delta E_A{}^U$. In the ground state of **3**, two allyl carbon atoms are members of a cyclopropane ring rich in p character. The change in the hybridization of these atoms on going from the ground to the transition state is, consequently, small. At the other end of the allyl moiety, the shortening of the distance, d, on passing to the transition state is smallest; the decrease in the s character of the hybridized orbitals on these carbon atoms is also small. These effects are found in the least change in $\Delta E_A{}^C$ value for the rearrangement of **3**. Thus, as far as the one-center terms are concerned, the ease of rearrangement is predicted to be in the order **4**>**1**>**3**, which is just the opposite of that determined by the total contributions to the activation energy.

It will, therefore, be seen that the greater facility of reaction in **3** compared with that of **1** and, more especially, with that of **4** is due to a large decrease in the ΔE_{AB}^N terms. There are three factors which are conceivable as the origin of the large negative ΔE_{AB}^N value in **3**: i) the strength of the interaction linking two allyl groups, ii) the strength of the bonds in each allyl moiety, and iii) the relief of the ring strain. The first factor is expressed by the ΔE_{AB}^N value due to the a+d interaction at the two ends of the allyl groups; it amounts to +0.914, −1.701, and −5.450 for the rearrangement of **3**, **1**, and **4**, respectively. The stabilizing order is in harmony with the decreasing atomic distances linking the two ends of the allyl moieties in the transition state, but is, again, opposite to the net order of the relative stability of the transition state. Secondly, the ΔE_{AB}^N between the atoms pertaining to the b and c bonds within the allyl group in **1′** and **1** (+1.258 eV) is much more than that in **3** (−1.763) and much less than that in **4** (+3.666). The destabilizing effect in the rearrangement of **4** can be interpreted in terms of the relatively long b (c) distance in the transition state. The corresponding b(c) distances in the transition state of **1** and **3** are, however, nearly the same at *ca.* 1.39 Å, which is the average C–C bond length of the order of 1.5; they are typified by those of benzene. A simple atomic distance *vs.* ΔE_{AB}^N argument does not hold in this case. As has been pointed out in Section (C), the allyl groups in **1′** are not planar any longer. A more careful examination of the **1′** structure reveals that

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[17] R. Criegee and R. Huber, *Chem. Ber.*, **103**, 1855 (1970).

[18] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

[19] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

the formally unpaired fourth valences of C_3 (C_5, C_6, and C_8 also) are not 2p orbitals but are $sp^{4.4}$ hybridized.[20] Moreover, they are directed to the opposite side of the $C_3C_4C_5$ ($C_6C_7C_8$) plane, inwards at the C_3 (C_5, C_6, and C_3) end and outwards at the C_4 and C_7 centers. The π-type overlap between the adjacent carbon atoms is necessarily inefficient, and the destabilization of **1′** relative to the transition state of **3** results in spite of a similar bond length b(c) (see Fig. 3).

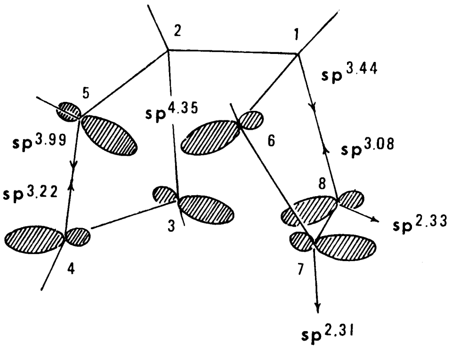

Fig. 3. Hybridization of the carbon atomic orbitals in **1′**.

Although it is not simple to define the strain energy by the E_{AB} of a specific bond, the E_{AB}^{N} (a, b, c) values in the ground state can be taken, in a sense, as a good measure of the intrinsic strain energy of these bonds, while ΔE_{AB}^{N} (f+g) may reflect the relief of the ring strain. We may note that the a bond in the cyclopropane ring of **3** is clearly weak when compared with those of **1** and **4**. The ΔE_{AB}^{N} due to bonds f and g is +0.099 and −0.050 for **1** and **3** respectively, and the stabilization of the transition state relative to the ground state is indicated. Thus, the relief of the ring strain seems to be another factor in the ease of rearrangement in **3**. The effect is not obvious in **1**.

(E) Intramolecular [2+2] Cycloaddition of 1 to Give Cubane. Several reaction paths from **1** leading to cubane were investigated in which the decrease in the cyclobutane/cyclobutene dihedral angle ($\Delta\theta$) from 119° to 90° was followed by changes in C–C bond lengths (Δr) and C–C–H bond angles ($\Delta\varphi$) according to a suitable function of $\Delta\theta$ (Eq. (10)). The general trend

$$\Delta r,\ \Delta\varphi \propto f(\Delta\theta) \qquad (10)$$

in the total energy *vs.* $\Delta\theta$ curve does not depend greatly on the type of f ($\Delta\theta$) as long as the latter is reasonably chosen by model considerations. Figure 4 shows a typical example in which $f(\Delta\theta)=\Delta\theta$. Strictly speaking, however, the lengthening of the ethylenic double bonds and the displacement of the vinylic hydrogen atoms out of the trigonal planes appear to lag befind $\Delta\theta$ as the reaction proceeds in the energy minimum cross-section of the potential energy hypersurface interrelating **1** and cubane. The energy value rises steadily during the course of the reaction untill just before the end of change in the dihedral angle (at *ca.* 98°), when it starts to fall to the value corresponding to the heat of formation of cubane. At the same time the bond lengths r's, and the bond angles, φ's, change suddenly to values more or less close to those of cubane. The Wiberg's bond indices between atoms pertaining to bond formation and bond cleavage also change abruptly at this point of the reaction coordinate. We obtain a separate energy *vs.* $\Delta\theta$ plot when the reaction starts from cubane to **1**. All these trends indicate that the reactions refuse to occur when an attempt is made to force them, and provide a typical example of *anti*-aromatic reactions in the electronic ground state.[21–23]

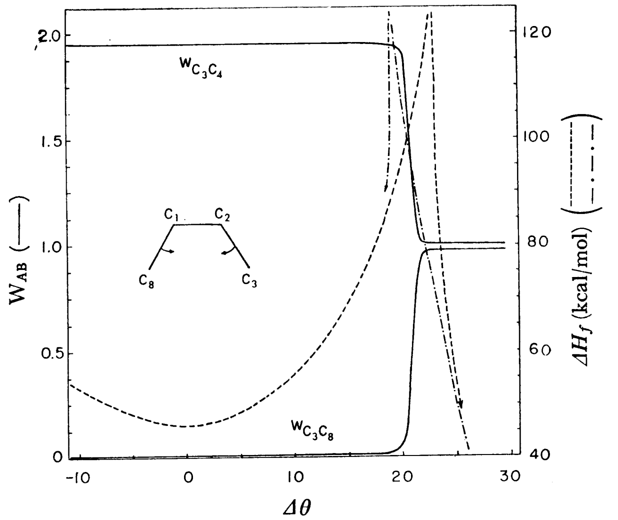

Fig. 4. The energy and the Wiberg's bond indices *vs.* $\Delta\theta$ plots for the ring closure of **1** ($\Delta\theta$=0) to give cubane ($\Delta\theta$=29.0°).

The authors wish to acknowledge stimulating discussions with Professor M. Ōki. They are also indebted to the Ministry of Education for financial support of this work.

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20) For the definition of the p character in individual hybrids in terms of the bond index of Wiberg, see C. Trindle and O. Sinanoglu, *ibid.*, **91**, 853 (1967).

21) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4291 (1971).

22) A rectangular disposition of the C_3, C_4, C_7, and C_8 and the C_{2v} symmetry as a whole, are assumed for the species throughout the reaction paths. The distortion from this geometry to a rhombic arrangement of the ethylenic carbon atoms with the total symmetry of C_2 results in the stabilization of the [2+2] interaction by means of the Jahn-Teller effect (see, *e.g.*, H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972)). However, the effect is expected to be counteracted by energy loss due to bond bending in the σ framework of the four-membered rings and, therefore, is not taken into present consideration.

23) Note added in proof. R. Gleiter, E. Heilbronner, M. Hekman, and H.-D. Martin, (*Chem. Ber.*, **106**, 28 (1973)) have reported the photoelectron spectral data and the molecular orbital analyses of **1** and **2**. Their results are in good agreement with ours.