March, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 841—846(1972) 841

The Cope Rearrangement of Bridged Homotropilidenes Studied by MINDO Methods[1]

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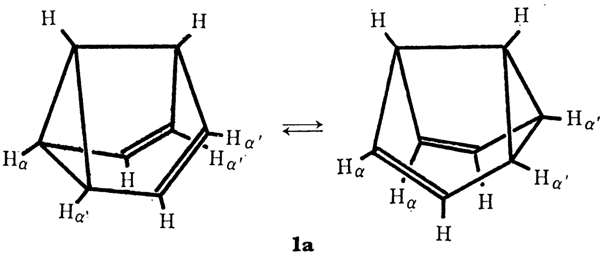
(Received July 2, 1971)

The theoretical structures and heats of formation of semibullvalene (**1a**), barbaralane (**1b**), and bullvalene (**1c**) have been investigated by the MINDO methods. The strain energies are estimated to be 19.7, 8.8, and 0.5 kcal/mol, respectively. The activation energies for the Cope rearrangement of these bridged homotropilidenes were obtained by a comparison of the results of a similar study on the biallylic transition states for the rearrangement. They are in good agreement with the experimental values. Extremely facile rearrangement in **1a** is attributed to the partial release of strain energy through the formation of the transition state, and to the proximity (2.16 Å) of the non-bonded termini of the divinylcyclopropane unit in the ground state.

Semibullvalene (**1a**) is unique for its extremely facile Cope rearrangement. The activation energies for the Cope rearrangement of homotropilidenes generally fall into the range 12±1 kcal/mol when they are bridged by a chain of two carbon units as in bullvalene (**1c**) and dihydrobullvalene. One carbon bridged homotropilidenes undergo rearrangement more easily; barbaralane (**1b**) and barbaralone have an activation energy of *ca.* 8 kcal/mol.[2] The NMR spectrum of **1a** consists of only three multiplets at δ 2.97, 5.08, and 4.17 ppm in the intensity ratio of 2:2:4, indicating that the chemical shift between the protons α and α' is averaged out in the time scale of NMR spectroscopy. The spectral pattern remains unchanged even at −100° at 100 MHz.[3] The activation energy of the degenerate Cope rearrangement represented by the following equation is thus expected not to exceed 5 kcal/mol.

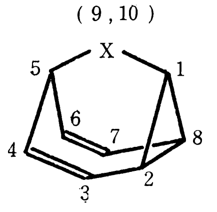


1a

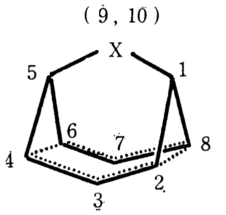
With no experimental technique available for obtaining further kinetic information on **1a**, and in view of recent success in the quantitative evaluation of the heat of formation by the all valence electron SCF MO theory at various levels of sophistication,[4] we adopted this theoretical tool to clarify the structural uniqueness of semibullvalene which causes the lower barrier to the Cope rearrangement.

Method of Theoretical Calculation

In order to evaluate the activation energy for the Cope rearrangement theoretically, it is necessary to calculate and compare the total energy or heat of formation of the ground state and the corresponding transition state of the bridged homotropilidenes. Since the rearrangement is degenerate, the transition state geometry should be symmetric with respect to the plane passing through the center of X and the carbon atoms numbered 3 and 7 as represented by **2a**—**c**, of which there is no *a priori* information as regards the precise geometry. Even the ground state conformation of the bridged homotropilidenes **1a**—**c** has not been reported except for bullvalene.[5] The equilibrium geometry should be determined by minimizing the molecular energy with respect to all the bond lengths and angles for the ground state as well as the biallylic transition state.



1a, X=zero carbon bridge
1b, X=CH_2
1c, X=CH=CH



2a, X=zero carbon bridge
2b, X=CH_2
2c, X=CH=CH

In principle, optimization of geometry has to be made with respect to 3N−6 internal coordinates. Although the number of the unknown is cut down considerably by the symmetry of the molecule, the computation time required would still be too long. As an example, reasonable assumption of C_s symmetry of **1a** still leaves the number of degree of freedom as 23. Fortunately we are allowed to take many of the bond lengths to be fixed to the standard values. In an extreme case, we may start with the standard bond lengths to effect faster

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[1] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971. Studies of Reaction Mechanism by All-Valence-Electron Semi-Empirical SCF-MO Theories. III. For paper II of the series note: H, Iwamura, K. Morio, and T. L. Kunii, *Chem. Commun.*, **1971**, 1408; I: H. Iwamura, K. Morio, M. Ōki, and T. L. Kunii, *Tetrahedron Lett.*, **1970**, 4575.

[2] G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem.*, **77**, 774 (1965), and papers cited therein.

[3] H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

[4] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., (1969); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., New York, N. Y., (1970).

[5] B. Andersen and A. Marstrander, *Acta Chem. Scand.*, **21**, 1676 (1967).

approach to the final geometry. This is necessary, when the MINDO/1 approximation is to be used, becuase the method is parametrized to give the observed heat of formation accurately only with the use of fixed standard bond lengths of Baird and Dewar.[6)]

The methods employed here for calculating the geometry of **1** and **2** are based on the MINDO/2 approximation to the full SCF equations of Roothaan. A complete specification of this method together with a discussion of the approximations have been given.[7)] 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.[8)] The Jacobi method for diagonalization of the *F* matrices is replaced by the Householder method. The calculations were carried out to a level of self consistency where the change in energies and the maximum change in the bond order matrix were less than 0.0001 eV and 0.0004, respectively.

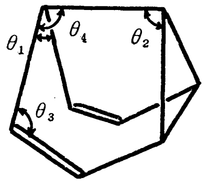


Fig. 1. Definition of angles changed as variables.

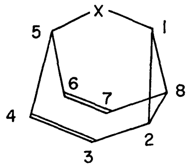
The procedure for calculating the geometry is exemplified by **1a**. Essentially the heat of formation was calculated for a systematically chosen set of bond angles shown in Fig. 1, and then minimized graphically. A set of numerical values were assigned to θ_1 to θ_4 and the coordinates of atoms were calculated using the standard bond lengths. The initial set of the angles was measured on molecular framework models of Prentice Hall, Inc.[9)] Angle θ_1 was first adjusted by minimizing the molecular energy. Angles θ_2, θ_3, and then θ_4 were similarly calculated with the computed value for θ_1. θ_1 was recalculated with the new values for θ_2 through θ_4. The process was repeated until an absolute minimum in energy was obtained within 1° with respect to all bond angles. The coordinates for H_1 and H_5, the protons attached to C_1 and C_5, respectively, were similarly adjusted on the mirror plane of the molecule. The coordinates for H_3 and H_4 were calculated by assuming that they lie in the $C_2C_3C_4$ and $C_3C_4C_5$ planes, and the C_3–H_3 and C_4–H_4 bonds bisect the $C_2C_3C_4$ and $C_3C_4C_5$ angles, respectively. Finally optimization with respect to the carbon to carbon bond lengths was carried out. Since the optimized bond lengths always differ from the standard values by less than 1%, the change in the bond lengths is considered not to affect the optimized bond angles materially. In the MINDO/1 approximation, a value of 1.09 Å was assumed for all C–H bonds except 1.08 Å for the vinylic C–H bonds. All the C–H bond legths were uniformly shifted by +0.1 Å in the MINDO/2 calculations as suggested by Baird *et al.*[6),7)]

As to the conformation of the transition state **2a**—**2c**, the bond lengths of C_1–C_2 and C_2–C_3, the interatomic distance C_1C_5, θ_1, θ_2, and θ_3 were taken as variables. θ_1 is defined as the angle between the planes $C_1C_2C_4C_5$ and $C_5C_6C_8C_1$. Displacement of C_3 and C_7 out of these planes, respectively, is expressed in terms of θ_2.

Results for Ground State Geometry

The theoretical structures for **1a**—**1c** are summarized in Table 1 together with the bond indices of Wiberg.[10)] As the method is intended for calculation of the ground state geometry for which no experimental information is so far available, or of the transition state geometry which is not amenable to experimental investigation, it is desir-

Table 1. Ground state geometries and bond indices of the bridged homotropilidenes determined by the MINDO/2 method

		C_1C_2	C_2C_8	C_2C_3	C_3C_4	C_4C_5	C_4C_6[a)]
1a	Bond distances (Å)	1.512	1.510	1.481	1.340	1.530	2.158
	Bond indices	0.9277	0.8791	1.0129	1.8448	0.9405	0.0595
		(0.8906	0.8129	0.9130	1.7678	0.8652	0.0466)[b)]
1b	Bond distances (Å)	1.512	1.510	1.480	1.339	1.530	2.327
	Bond indices	0.9291	0.8931	1.0049	1.8690	0.9541	0.0280
		(0.8806	0.8468	0.8954	1.7850	0.8595	0.0263)[b)]
1c	Bond distances (Å)	1.510	1.510	1.483	1.336	1.529	2.527
	Bond indices	0.9078	0.9078	0.9937	1.8834	0.9488	0.0113
		(0.8558	0.8558	0.8899	1.7855	0.8519	0.0211)[b)]

a) Atomic distances b) Bond indices by the MINDO/1 method

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6) 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).

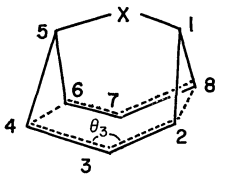
7) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); N. Bordor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

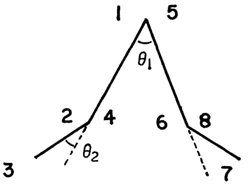
8) Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana 47401.

9) Prentice Hall, Inc., Englewood Cliffs, N. J.

10) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968). The bond index is defined as the sum of the squares of the bond orders (P_{jk}).

Table 2. Transition state geometries and bond indices of Wiberg calculated by the MINDO/2 method





		C_1C_2	C_2C_3	C_2C_8	C_3C_7	Bond angles (°)		
						θ_1	θ_2	θ_3
2a	Bond distances (Å)	1.520	1.400	1.771	2.844	73	5	110.0
	Bond indices	0.9079	1.3853	0.4566	0.0987			
		(0.8588	1.3193	0.4032	0.0700)[a]			
2b	Bond distances (Å)	1.524	1.405	1.798	2.768	72	6	117.5
	Bond indices	0.9214	1.3821	0.4513	0.0936			
		(0.8540	1.3056	0.4023	0.0713)[a]			
2c	Bond distances (Å)	1.520	1.395	1.770	2.587	72	6	124.0
	Bond indices	0.9128	1.3796	0.4503	0.0957			
		(0.8424	1.3006	0.3999	0.0701)[a]			

a) Bond indices by the MINDO/1 method

able to test the computational method with molecules of known geometry. The calculated bond lengths in the cyclopropane rings of **1a**—**c** are uniformly 1.510 Å and are considerably shorter than 1.544 Å experimentally obtained for bullvalene.[5] They are, however, in good agreement with those usually observed in the cyclopropane derivatives.[11] The adjacent C_2C_3 distance of **1c** is optimized at 1.483 Å; the experimental value is smaller by 0.017 Å. The reason for the discrepancy is as yet not clear. Only for the consistency of comparison, the optimized geometry is adopted in the following discussion.

One of the most significant differences in the ground state geometries of **1a**—**c** is revealed by the interatomic distances C_4C_6 ($=C_2C_8$). They are 2.158, 2.327 and 2.527 Å, for **1a**, **1b**, and **1c**, respectively; the order of bond indices is **1a**>**1b**>**1c**. Since the distances should eventually be reduced to *ca.* 1.51 Å to form a carbon-carbon single bond of the cyclopropane ring in the course of the Cope rearrangement, it is interesting that from the present calculation the ground state of **1a** is already forced towards the geometry of the transition state **2a**, while **1b** is less, and **1c** is least perturbed in the direction of the respective transition states.

Results for Transition State Geometry

The optimized geometries of **2a**—**c** are collected in Table 2. It is noted that, contrary to the ground state geometry in which the angle between the wings of the divinylmethane moiety ($C_4C_5C_6$) is in the order **1a**< **1b**<**1c**, θ_1 defined as the dihedral angle between the two allylic planes is almost constant at 72° throughout the transition states **2a**—**c**. Their C_2C_8 ($=C_4C_6$) distances differ by not more than 1%. The result suggests that the energy of the transition states **2a**—**c** basically does not differ. The mode in which the total molecular energy depends on the dihedral angle θ_1 is illustrated in Fig. 2 It is apparent that the potential energy curve is considerably steep on both sides of the equilibrium geometry. A bond population analysis reveals that the energy minimum is reached as a result of an intricate balance between the bonding interaction of both termini of the biallylic systems which stabilizes the transition state to a greater extent as θ_1 decreases and the anti-bonding interaction of the *p*-orbitals on C_3 and C_7 which destabilizes the internal energy. To the latter has to be added the strain energy produced in the angle $C_2C_1C_8$ and $C_4C_5C_6$ as θ_1 decreases. A similar argument based on the simple Hückel approximations has been proposed by Fukui and Fujimoto for preference to the chair-like conforma-

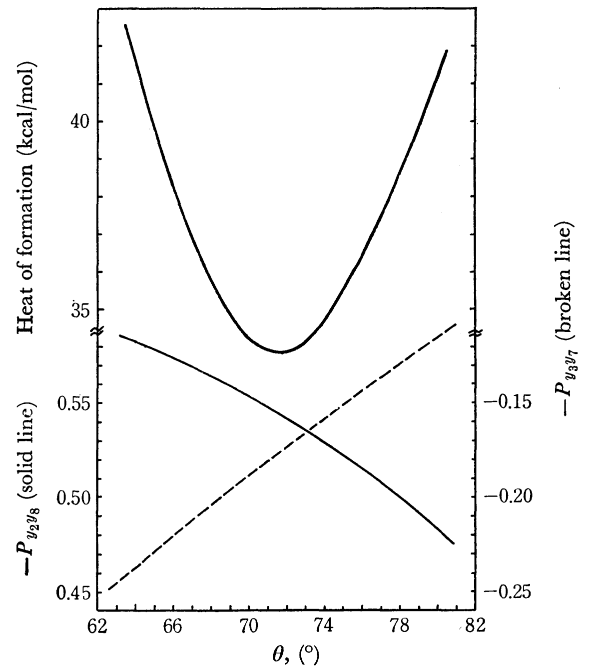


Fig. 2. Heat of formation and bond orders, $P_{y_2y_8}$ (between the $2p_y$ orbitals of C_2 and C_8, the y axis being in the direction $\overrightarrow{C_2C_8}$) and $P_{y_3y_7}$, *vs.* θ_1 for **2b**.

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[11] E. Goldish, *J. Chem. Educ.*, **36**, 408 (1959).

tion of the transition state for the Cope rearrangement,[12] while Woodward and Hoffmann explained the effect in terms of the orbital symmetry.[13] This orbital repulsion effect first suggested by Doering and Roth[14] also explains why the carbon atoms 3 and 7 tend to be out of the planes defined by $C_1C_2C_4C_5$ and $C_5C_6C_8C_1$, respectively, in the equilibrium geometries of **2**. The average deviation of 6° seems enough to bring the distance between C_3 and C_7 apart without suffering from loss of total conjugative stabilization energy in each allylic group and from strain produced in the ring systems.

TABLE 3. HEATS OF FORMATION AND STRAIN ENERGIES OF THE HOMOTROPILIDENES **1a**—**c** CALCULATED BY THE MINDO METHODS

	Heats of formation (kcal/mol)			Strain energies (kcal/mol)
	MINDO/2	MINDO/1	Franklin's group additivity	
1a	27.1	53.0	33.3	19.7
1b	15.5	37.2	28.4	8.8
1c	38.4	52.8	52.3	0.5

Results for Heat of Formation and Charge Distribution of the Ground States 1a—c

Heats of formation corresponding to the equilibrium geometries optimized by the MINDO/2 method and given in Table 1 are listed in Table 3. Border *et al.* reported a value of 42.0 kcal/mol by applying the MINDO/2 method to the observed geometry of bullvalene.[15] The energy minimization along the line outlined in the previous section resulted in heat of formation of 38.4 kcal/mol for bullvalene with the normal 1.51 Å for the C–C bond length of the cyclopropane ring.

In the third column of Table 3 are given heats of formation calculated by the MINDO/1 version on the geometries of the same bond angles determined by the MINDO/2 method. Bond lengths are, however, shifted from the optimized ones to the standard values originally proposed by Baird and Dewar.[6] The MINDO/1 method is considered to give better results as far as heat of formation is concerned.[6,7]

By applying Franklin's group additivity method,[16] heats of formation were estimated for the ideal strain-free molecules corresponding to **1a**—**d**. The difference between the molecular energies obtained by the MINDO/1 method and those computed by Franklin's method can be regarded to give good estimate for the strain energy of these hydrocarbons.

The charge distributions and resultant dipole moments for the homotropilidenes **1a**—**c** calculated by the two MINDO methods are summarized in Table 4.

Results for Heat of Formation and Charge Distribution of the Transition States 2a—c

The optimized heats of formation of the biallylic structures **2a**—**c** representing to the transition states for the Cope rearrangement are listed in Table 5. For the MINDO/1 predictions of the transition state energies, ambiguity remains in the choice of the C_2C_3 bond length. Although it should not be far from 1.40 Å optimized by the MINDO/2 version, we do not know which length will give most accurate heats of formation by the MINDO/1 parametrization.[6] In Fig. 3 is illustrated how heats of formation predicted by the MINDO/1 method depend

TABLE 4. ELECTRON DENSITIES AND THE RESULTANT DIPOLE MOMENTS OF **1a**—**c** DETERMINED BY THE MINDO METHODS

Atom	1a		1b		1c	
	MINDO/1	MINDO/2	MINDO/1	MINDO/2	MINDO/1	MINDO/2
C_1	3.997	4.018	3.976	3.995	3.917	3.954
C_2	3.905	3.940	3.917	3.951	3.917	3.954
C_3	3.987	4.020	3.972	4.006	3.964	3.993
C_4	3.991	3.995	3.990	4.009	3.993	4.015
C_5	3.864	3.921	3.880	3.924	3.845	3.905
C_9	—	—	3.827	3.924	3.993	4.015
H_1	1.045	1.013	1.047	1.020	1.068	1.029
H_2	1.064	1.029	1.066	1.030	1.068	1.029
H_3	1.038	1.014	1.039	1.011	1.048	1.016
H_4	1.021	1.006	1.043	1.015	1.035	1.011
H_5	1.081	1.039	1.065	1.033	1.080	1.039
H_9	—	—	1.076	1.030	1.035	1.011
			Dipole moments			
Point charge	0.216	0.071	0.131	0.179	0.155	0.172
Hybridization	0.096	0.141	0.105	0.074	0.181	0.146
Sum	0.310	0.137	0.026	0.192	0.026	0.318

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12) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, **1966**, 251.

13) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p. 148.

14) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); *Angew. Chem.*, **75**, 27 (1963).

15) N. Bordor, M. J. S. Dewar and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970).

16) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

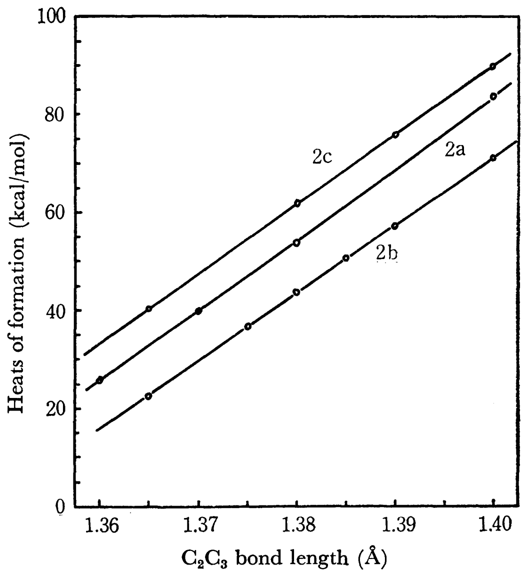

Fig. 3. Dependence of heats of formation by the MINDO/1 method on the C_2C_3 bond length in **2a**—**2c**.

on the C_2C_3 bond length. Although the curves show neither minima nor maxima in the region in question, it is noted that the difference in heats of formation between **2a**—**c** is independent of the choice of the C_2C_3 bond lengths. The numerical values of heat of formation arbitrarily obtained at the intercept of the curves in Fig. 3 at C_2C_3=1.38 Å are listed in the third column of Table 5.

Franklin's group additivity method is now employed to calculate the heats of formation of X part of **2a**—**c**, they are 0, —4.9, and 19.0 kcal/mol, respectively. By subtracting the latter from the heats of formation predicted by the MINDO/1 method, the partial molecular energies due to the biallylic portion of **2a**—**c** are estimated.

Table 5. Heats of formation of the transition states **2a**—**c** for the Cope rearrangement

	MINDO/2	Heats of formation (kcal/mol) MINDO/1 (C_2C_3=1.38 Å)	Biallyl moiety
2a	45.4	53.6	53.6
2b	33.8	43.9	48.8
2c	64.8	61.9	42.9

In view of the similar distances between the two allylic moieties in **2a**—**c** as listed in Table 2, we assume that the stability derived from resonance coupling between the two allylic portions does not differ much in **2a**—**c**. A slight difference in stability which is in the order **2a**<**2b**<**2c** in the last column of Table 5 can be attributed to varieties in the strain energy due to the deformation of the "sp^2" hybridized carbon atoms, C_2, C_3, and C_4 in the transition states.

The electron densities and the resultant dipole moments for the transition states **2a**—**c** calculated by the two versions of the MINDO methods are summarized in Table 6.

Discussion on the Origin of Different Activation Energy for Values the Cope Rearrangement

We now arrive at the theoretical activation energy for the Cope rearrangement of the bridged homotropilidenes by comparing the heats of formation of the ground states **1a**—**c** with those of the transition states **2a**—**c**. The results are shown in Table 7. Note that the MINDO/1 method reproduces almost quantitatively the activation energies for the rearrangement. A satisfactory agreement is not unexpected since it is generally accepted that special effort is made during parametrization of the MINDO/1 approximation towards the reproduction of heats of formation.[6)] The results of the MINDO/2 approximation are on the contrary less quantitative, and the deviation might be due to underestimation of the strain energy of the cyclopropane ring; the calculated heat of formation of cyclopropane is 3.8 in marked contrast to the observed 12.7 kcal/mol.[6,7)] Thus the heats of formation of **1a**—**c** are underestimated relative to **2a**—**c** which have no such strain, with the consequent elevation in the calculated activation energies by the MINDO/2 method.

Table 6. Electron densities and the resultant dipole moments of **2a**—**c** determined by the MINDO methods

Atom	**2a** MINDO/1	**2a** MINDO/2	**2b** MINDO/1	**2b** MINDO/2	**2c** MINDO/1	**2c** MINDO/2
C_1	3.889	3.953	3.892	3.948	3.866	3.942
C_2	3.985	3.980	3.987	3.978	3.972	3.962
C_3	3.976	4.037	3.964	4.042	3.974	4.050
C_9	—	—	3.832	3.921	3.971	3.996
H_1	1.069	1.021	1.054	1.023	1.083	1.039
H_2	1.029	1.010	1.044	1.018	1.039	1.011
H_3	1.037	1.008	1.039	1.006	1.056	1.021
H_9	—	—	1.072	1.029	1.028	1.006
			Dipole moments			
Point charge	0.378	0.455	0.893	0.699	1.090	0.584
Hybridization	0.731	0.813	0.919	0.753	1.000	0.889
Sum	0.353	0.359	0.026	0.054	0.090	0.305

Satisfactory reproduction of the activation energies

Table 7. Activation energy for the Cope rearrangement

	Activation energy (kcal/mol)		
	MINDO/1	MINDO/2	obsd
Semibullvalene (**1a**)	0.6	18.3	<5[3]
Barbaralane (**1b**)	6.7	18.3	8.76[2,17]
Bullvalene (**1c**)	9.1	25.4	11.8[18]

by the present SCF MO calculations is surprising in view of the fact that the experimental data are obtained in the condensed phase while the calculation is applied to the isolated molecules in a vacuum. Success can partly be ascribed to special situation where there is no significant deviation of electric charge from even distribution in **1a**—**c** as well as in **2a**—**c** (Tables 4 and 5).

From the NMR spectral behavior of **1a**, it could be postulated that semibullvalene might have the mesovalent structure **2a**.[3] However, this can be easily ruled out by the normal UV spectrum of **1a**.[3] It is supported on theoretical ground that semibullvalene has no such novel bonding but only facile Cope rearrangement. Recently, Anet obtained the value of 6.4 kcal/mol as the activation energy for the Cope rearrangement of the octamethyl derivative of **1a**.[19] The effect of methyl substitution in enhancing or retarding valence isomerization is not uncommon. Complete thermal conversion from cyclooctatetraene to semibullvalene can be achieved only when they are fully methylated,[20] while the interconversion is less efficient in the tetramethyl derivatives.[21] No effort has so far been successful in the parent semibullvalene. In the present case, the effect of the methyl substitution can be rationalized by considering a greater planarity of the five membered ring of C_1 through C_5 in the transition state than in the ground state; the eclipsing methyl groups are sterically more demanding than the more or less staggered orientation.

With respect to the origin of different acitvation energies for the Cope rearrangement of these bridged homotropilidenes,[22] we note from Table 3 and 5 that the strain energies in the ground state are sharply in the order **1a**>**1b**>**1c**, while those of the transition state are moderately in the order **2a**>**2b**>**2c**. Thus it is concluded that one of the possible factors contributing to the different activation energies stems from the strain energies of the ground state of these hydrocarbons. We see from Table 1 and 2 that the bond between carbons 4 and 6 ($=C_2C_8$) in the transition states is conventionally represented by the dotted line, and the bond index is easily expected to be one half; the calculated values by the MINDO/2 methods are 0.46, 0.45, and 0.45 for **2a**, **2b**, and **2c**, respectively. The corresponding values in the ground states, **1a**, **1b**, and **1c**, are 0.06, 0.03, and 0.01, respectively. Although no strict proportionality holds *a priori* between bond indices and bond formation, we can say as a first approximation that the Cope rearrangement has already taken place *ca.* 13% ($=0.06/0.46\times 100$) in **1a** to the forward direction of the reaction coordinate. The effect is less pronounced in **1b**, and almost negligible in **1c**.[22]

The authors are indebted to the Ministry of Education for financial support of this work.

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