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THE SEMIBULLVALENE QUESTION

A

SEMI-EMPIRICAL MOLECULAR ORBITAL AND BOND ENERGY APPROACH

BY

SHIOW YEH LEE, 1944-

A

THESIS

submitted to the faculty of

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Dedicated to My Parents

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ABSTRACT

Semi-empirical molecular orbital calculations of the Extended Huckel and MINDO/1 type have been performed on semibullvalene and the supposed transition state for its degenerate [3,3] sigmatropic rearrangement. The results have been coupled with bond energy calculations to ascertain whether semibullvalene is homo-aromatic or is undergoing a rearrangement of exceedingly low activation energy. A preponderance of the resulting data suggests that semibullvalene is homo-aromatic.

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THE SEMIBULLVALENE QUESTION

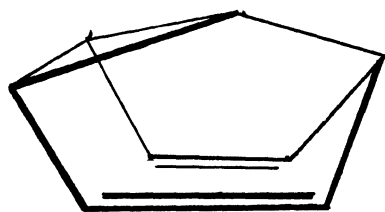
Summary: Semi-empirical molecular orbital calculations of the Extended Huckel and MINDO/1 type have been performed on semibullvalene and the supposed transition state for its degenerate [3,3] sigmatropic rearrangement. The results have been coupled with bond energy calculations to ascertain whether semibullvalene is homo-aromatic or is undergoing a rearrangement of exceedingly low activation energy. A preponderance of the resulting data suggests that semibullvalene is homo-aromatic.

The extensive investigations of Doering and coworkers¹ into the nature of the Büchner esters¹ and subsequently into degenerate Cope rearrangements,² has stimulated numerous chemical and some theoretical studies.^{3,4} Woodward and Hoffmann⁵ have formulated elegant empirical rules applicable to such processes. More recently, Brown, Dewar and Schoeller⁶ have examined the stereochemistry of the Cope rearrangement of biallyl using the MINDO/2 method.

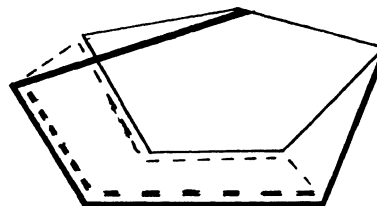
The present study was undertaken prior to the general availability of MINDO/2⁷ and involves a comparison of MINDO/1⁸, extended Huckel (EXHUC)⁹ and bond energy calculations. The choice of semibullvalene as a model system was dictated by the unusual properties observed for its apparent 1-aza analog¹⁰ and by the failure of Zimmermann and Grunewald¹¹ to observe any variable temperature nmr phenomenon down to -110° for semibullvalene.

Simple energy considerations and logic would suggest that semibullvalene is (II) and not (I) as originally assigned. It is worth noting

that Zimmerman and Grunewald¹¹ excluded (II) as a possibility on the



I



II

basis that the ultraviolet spectrum resembled that of dihydrobullvalene. This argument would appear tenuous in light of the fact that non-conjugated dienes of suitable geometry exhibit uv maxima but no one has determined what maximum should arise from a homo-aromatic species such as (II). The absence of a phenomenon is not evidence for its existence and in this case there is sufficient a priori evidence to suggest that (II) might be a better representation than (I) in some if not all cases where "average" nmr spectra have been observed.

The distinction between (I) and (II) will require careful spectroscopic analyses. Even if a variable temperature nmr spectrum were ultimately observed, there is no guarantee that the situation is the same at room temperature as that observed at -150° . As early as 1888 Le Chatelier recognized that equilibria are altered in a systematic fashion by changing temperature. Although (I) undergoing degenerate rearrangements at -150° might be observed, (II) could be the predominant form at 40° . It is clear from the nature of exchange phenomena,

that the activation energy for the rearrangement, if present, cannot exceed 5 Kcal./mole.^{*,12} To distinguish between (I) and (II) by spectroscopic means will require distinguishing between C_{1V} and C_{2V} symmetry.

An alternate approach to demonstrating the existence of a homoaromatic species involves the demonstration of a diamagnetic exaltation.^{13,14} Such a phenomenon is considered to be evidence of a ring current. Unfortunately, cyclopropanes behave somewhat anomalously and such experiments involve determination of a calculated diamagnetic susceptibility for the molecule (I) and then ascribing any deviation to special properties of the system.

A chemical proof is equally tenuous. The perturbations resulting from bringing a reagent molecule near semibullvalene may well force the molecule to adopt a particular configuration unrelated to the ground state. This would lead to contradictory results. Of particular note is the panoply of chemical and physical results which have resulted from the study of the norcaradiene-tropilidene problem.¹⁵

The true nature of semibullvalene may be discernable using variable temperature C^{13} magnetic resonance studies.¹² However, suitable instrumentation is not universally available.

The semibullvalene problem therefore lends itself nicely to semi-empirical molecular orbital approaches. The major prerequisite is the availability of a method of sufficient reliability. The MINDO/1 method appears** to be suitably reliable and on occasion the EXHUC method has furnished useful qualitative results in spite of its inherent weakness.

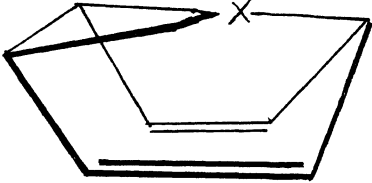



*Calculated using equations described in Chapter 9, of reference 12.

**Although Dewar strives for errors of ± 1 Kcal/mole, we have chosen on the basis of calculations on perhydro-pentalene to assume an accuracy of ± 10 Kcal/mole. MINDO/1 predicts $\Delta H_f^{298} = +8.022$ Kcal./mole whereas

The compound semibullvalene (C_8H_8) was first isolated by Zimmermann and Grunewald¹¹ and subsequently others have prepared related compounds.¹⁶ In several instances observed nmr phenomena were equally consistent with the assignments of Type (I) or of Type (II) structures if one assumed that Type (II) molecules were undergoing rapid reversible sigmatropic rearrangements of the homo-tropilidene type. In those cases where average nmr spectra were observed, the spectra exhibited no temperature dependence. Attempts at extrapolation of activation parameters from known degenerate sigmatropic rearrangements of structurally similar compounds (III) (Table 1) are unsatisfying because the principle question involves evaluation of the relative strain energies of Type (I) and (II) structures. If the difference is as great as 8-10 Kcal, the internal energies of Type (I) and (II) structures will be comparable, and if all other energy terms remained equal they would be equally probable. However the symmetry of the systems differ and we can therefore assume that the more symmetrical system (II) will be preferred. The interesting possibility arises that by suitable substitutions, it will be possible to synthesize compounds of either type and examine rate processes for reactions having vanishingly small activation parameters when suitable instrumentation becomes available.

**the reported value (S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey and R. N. Boyd, J. Amer. Chem. Soc., 1970, 92, 3109) report 22.3. It seems doubtful that more than 10 Kcal derives from non-systematic errors. Hence the differences between (I) and (II) are much better than the absolute numbers.

Table 1
ACTIVATION PARAMETERS OF RELATED SYSTEMS

x =	 III			Ref.
	E_a^- Kcal./mole	ΔH^\ddagger Kcal./mole	ΔS^\ddagger Gibbs	
-CH=CH-	11.5 \pm 0.1	10.9 \pm 0.1	-4.8 \pm 0.4	a
	12.9 \pm 0.2			b
CH ₂ -CH ₂	12.6 \pm 0.4	12.0 \pm 0.4	+11.0 \pm 4	c
C=O	8.1 \pm 0.4			d
CH ₂	10.4 \pm 0.3	9.8 \pm 0.3	+11.5 \pm 0.3	e
	13.2 \pm 0.6			b
	12.7 \pm 0.4			b

References: a) M. Saunders, Tetrahedron Letters, 1963, 1699; A. Allerand and H. S. Gutowsky, J. Amer. Chem. Soc., 1965, 87, 4092; b) J. F. M. Oth, J. M. Gilleo and R. Merenyi, cited by G. Schröder, J. F. M. Oth and R. Merenyi, Angew. Chem. Internat. Edit., 1965, 4, 752; c) J. F. M. Oth and J.-M. Giles, cited by G. Schröder and J. F. M. Oth in Angew. Internat. Edit., 1967, 5, 414; d) J. B. Lambert, Tetrahedron Letters, 1963, 1901; e) J. H. Hartenstein, cited by G. Schröder and J. F. M. Oth. loc cit.

DISCUSSION OF RESULTS

The recent work of Dewar on the calculation of heats of formation of strained hydrocarbons^{7,8} and the ready availability of the associated computer program along with the Extended Huckel (EXHUC) program of Hoffman^{9,18} offered an ideal chance to compare the two programs and their usefulness to the organic chemist. Calculations can be made here without prior knowledge of the experimental results and verification is possible without the necessity of undertaking long involved syntheses of questionably available molecules. In addition, the distinction to be made here will be sharp. The difference between (I) and (II) will probably amount to less than 10 Kcal./mole.

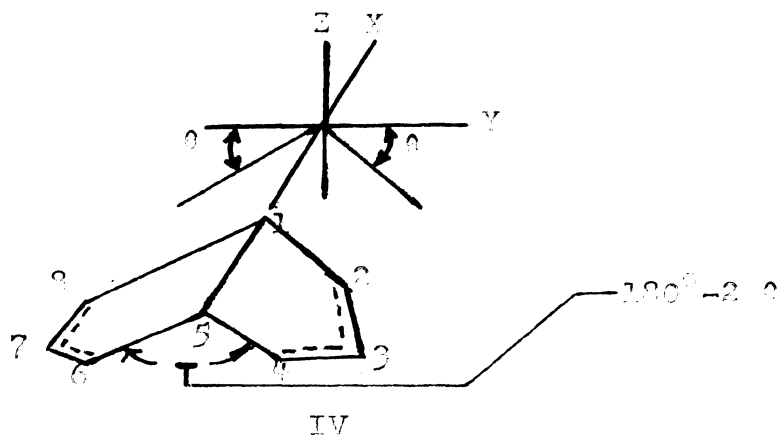
The most difficult part of these calculations is the derivation of the coordinants of the atoms and the determination of which bond lengths and angles will furnish a potential energy minimum. The problem is somewhat simplified in the case of MINDO/1 calculations in that Dewar⁸ specifies bond lengths on the basis of hybridization type, ring environment and neighboring atom hybridization. The EXHUC calculations are normally performed using experimental bond distances and angles, or lacking these, known values from structurally similar compounds. This approach will on occasion furnish misleading results if a bond length is altered by the nature of the molecule.

Dewar¹⁷ has on occasion criticized the EXHUC method pointing out that according to EXHUC the hydrogen molecule will have minimum energy when both atoms have the same coordinants. This point is of critical importance because EXHUC predicts bond shortening for (II). To check

the reliability in our system we calculated and found that EXHUC predicts the proper CC bond length for tropylium ion.¹⁹

The results obtained exhibit a significant dependence upon bond lengths and bond angles. In all cases involving EXHUC we have performed calculations using model bond lengths¹⁹ as well as those used by the MINDO/1 method. In addition bond angles were varied until a potential energy minimum was obtained. The resulting angles were then employed for both MINDO/1 and EXHUC calculations. The parameters employed with the programs were the same as the ones used by their authors. No attempt was made to improve on these to obtain "acceptable results". The bond parameters employed are summarized in Table 2.

The resulting energies in Table 3 were obtained for the supposed "ground state" (I) and for the "transition state" (II). It was assumed that (II) would have C_{2v} symmetry and that a potentially energy minimum should exist as a function of the angle θ (Figure VI) ($E_{\min}(\theta)$). A priori considerations lead to the conclusion that $E_{\min}(\theta)$ should occur at 45° . The EXHUC result was 43.6° . (Table 4)



¹⁹ A. I. Kitaigorodskii, Yv. T. Struckov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, Izvest. Akad. Nauk SSSR. Otd. Khim Nauk, 1960, 39; Chem. Abs. 56:11028c. Found a radius of 1.69Å for the carbon ring.

Table 2

BOND LENGTH AND ANGLE PARAMETERS EMPLOYED

METHOD	MINDO		EXHUC		MINDO/1		EXHUC	
	I	Å	I	Å	II	Å	II	Å
C ₁ -C ₂	1.514		1.520		1.520		1.412	
C ₂ -C ₃	1.520		1.530		1.397		1.408	
C ₃ -C ₄	1.483		1.337		1.397		1.408	
C ₄ -C ₅	1.520		1.530		1.520		1.412	
C ₁ -C ₅	1.534		1.541		1.534		1.440	
C ₁ -H ₁	1.093		1.080		1.093		1.098	
C ₂ -H ₂	1.093		1.070		1.084		1.091	
C ₃ -H ₃	1.083		1.070		1.084		1.090	
C ₄ -H ₄	1.083		1.070		1.084		1.091	
C ₅ -H ₅	1.093		1.080		1.093		1.098	
ANGLES (DEGREES)								
ANGLE								
C ₁ C ₂ C ₃	125.8		124.4		113.75		118.0°	
C ₂ C ₃ C ₄	109.6		106.5		115.0		117.6°	
C ₃ C ₄ C ₅	109.6		123.0		115.0		118.0°	
C ₄ C ₅ C ₁	121.01		117.7		119.7		120.2°	
C ₅ C ₁ C ₂	113.3		121.2		119.7		120.2°	
C ₂ C ₁ C ₈	60.0		60.0					
C ₄ C ₅ C ₆	120.0		120.0					
C ₃ Axis C ₇	89.5		89.8					
H ₁ C ₁ C ₅	114.47		120.47		114.47		120.0°	
H ₅ C ₅ C ₁	114.47		114.47		114.47		120.0°	

Table 3

ENERGIES OF I AND II AS A FUNCTION OF METHOD AND MODEL

Compound	(I)			(II)		
Model [#]	A	A	B	C	C	D
Method						
MINDO/1 [*]	+183.6 (-1600.28) ⁺			+141.3 (-1642.60) ⁺		
EXHUC ⁺		-17135.16	-17114.34		-17183.62	-17099.82

[#] Models A and C employ MINDO/1 bond lengths. Models B and D employ bond length from Chemical Society, Special Publications 11 and 18.

* H_f in Kcal./mole.

+ Total bonding energy in Kcal./mole.

Table 4

ANGULAR DEPENDENCE OF TOTAL BONDING
ENERGY FOR (II) BY EXHUC METHOD

MODEL	C	D	
θ°		θ	
35.00	-17167.03	35.00	-17080.92
40.00	-17180.58	40.00	-17096.31
43.35	-17183.58	42.00	-17099.23
43.50	-17183.62	43.00	-17099.75
43.60	-17183.61	43.20	-17099.77
43.7	-17183.55	43.40	-17099.77
45.00	-17183.05	43.50	-17098.81
50.00	-17168.30	44.00	-17099.60
55.00	-17114.66	44.50	-17099.18
60.00	-16986.46	45.00	-17098.64
		50.00	-17077.04
		55.00	-17007.60
		60.00	-16839.70

Values are in Kcal./mole

Calculations employing the MINDO/1 method were severely limited by practical considerations.* We therefore assume the a priori configuration for (II) corresponds with the potential energy minimum. The resulting value is appreciably lower than that calculated for (I) and may actually be too low. A better value may ultimately arise from subsequent calculations of this type. However, at present, there would appear to be little to argue which MINDO method should be employed. MINDO/1 tends to underestimate repulsion terms and MINDO/2 tends to furnish poor results with strained systems. From our calculations on perhydropentalene, it would appear that our values are ca. 10 Kcal/mole more endothermic than they should be.

In order to supplement these calculations we have therefore determined the energy of isomerization of (I) to (II) using a group contribution method in combination with simple Huckel calculations of the delocalization energy to be expected from a π system such as (II). The values for the resonance integrals, $\beta_{2,8}$ and $\beta_{4,6}$ were derived using the method of Coulson and Golebiewski while employing the values for $r_{2,8}$ and $r_{4,6}$ resulting from the EXHUC calculations of the ideal geometry for (II).²⁰

The process of going from (I) to (II) involves the attainment of the transition state for a Cope rearrangement. The activation energy for the simplest example, biallyl, is 35.5 Kcal./mole.²¹ The additional substitution of (I) can be expected to lower this value 2-4 Kcal./mole. The relief of strain energy in going from (I) to (II) will

*A single calculation on C_8H_8 systems required ca. 2.5 hours. An IBM 360-50 computer was used.

amount to at least 35 Kcal./mole.²² In addition the calculated delocalization energy for (II) is 6-10 Kcal./mole (calculated by HMO method with $\beta_{2,8}$ and $\beta_{4,6}$ corrected for increased distance and depending on the value employed for β_{cc} .²⁰

The choice as to which set of values to employ from the EXHUC calculations is of some import. In Hoffmann's original paper⁹, he pointed out that he arbitrarily choose typical bond lengths and did not attempt to obtain optimum values for the problems he considered because there are too many parameters to be varied in molecules lacking high symmetry. No experimental values are available for semibullvalene. Because of the symmetry associated with both (I) and (II) we made some attempt at arriving at the optimum configuration. The best values we obtained resulted from using the MINDO/1 distances and angles. This does not preclude the possibility that better values may exist. However, we feel forced to conclude that bond shortening does occur and this results have been reported by Baldwin²³ using EXHUC calculations and have been obtained in these laboratories on tropylium ion.

Thus it would appear that (II) is favored by at least 8 Kcal./mole over (I) and may actually be preferred by as much as 14 Kcal./mole.

All of the above treatments, with the exception of the EXHUC calculation which did not allow for bond length optimization, predict that semibullvalene is homo-aromatic and is best represented by structure (II).

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VITA

Shiow Yeh, daughter of Lai-chen and Feng Yeh, was born on June 24, 1944 in Taipei, Taiwan, China.

She received her primary and high school education in Taipei, Taiwan. She received a Bachelor of Science degree in Chemistry from National Taiwan Normal University, Taipei, Taiwan in June 1968. In January 1969, she attended the graduate school of the University of Missouri-Rolla.

On May 30, 1970, she married Mr. Kun-chieh Lee, son of Mr. and Mrs. Huey-chou Lee.

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