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Theoretical Study of a Symmetry-Allowed Dimerization of Benzene[1]

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Abstract: Semiempirical MNDO calculations of a symmetry-allowed dimerization of benzene are reported. The chemically bound C_s point-group dimer (*o,p'*-dibenzene) studied has the appearance of a 1,4-cyclohexadiene molecule bonded to 1,3-cyclohexadiene. The calculations augment results given earlier for four symmetry-forbidden dimerizations of benzene. The character of six stationary points on the $C_{12}H_{12}$ energy hypersurface is examined by use of the Hessian matrix. These points are (1) two benzenes **1**, (2) the stable C_s symmetry benzene dimer **2**, (3) a stable C_1 symmetry biradical **3**, (4) two C_1 symmetry transition states **4** and **5**, and a C_s symmetry "hill" **6**. MNDO predicts that the formation of the two new σ bonds on the lowest energy reaction path leading from **1** to **2** is asynchronous. The stationary point on a synchronous C_s symmetry path leading to **2** from **1** is a hill; i.e., there are *two* negative vibrational eigenvalues at this point. The points **3**, **4**, and **5** are shown to have biradical character by use of unrestricted Hartree–Fock (UMNDO) and 3 × 3 configuration interaction MNDO calculations; similar calculations on **1**, **2**, and **6** show that for these points a biradical description is less necessary. The activation barrier on the path from **1** to **2** via **4** and **5**, corrected for zero-point vibrational effects, is 55 kcal/mol. This is 40 kcal/mol less than that found for any of the symmetry-forbidden dimers. The MNDO energy of metastable **2** and **3**, corrected for zero-point effects, is 41 and 18 kcal/mol, respectively, higher than that of **1**. At the stationary points, some comparisons of the MNDO energies with ab initio minimal basis set SCF and group additivity energies are made.

I. Introduction

In previous work, we reported MNDO, ab initio, and group additivity studies of the formation of four chemically bound dimers (**7**, **8**, **9**, and **10**—see Figure 7) of benzene.[2a,2b] For related work also see ref 2c–2e. The formation of these four dimers from two benzene molecules **1** proceeds by symmetry-forbidden[3] reaction paths. Here, an MNDO[4] study of a benzene dimerization that proceeds by a symmetry-allowed path is reported; the reaction **1** → **2** is of the Diels–Alder (D–A) type (i.e., it is a [4 + 2] cycloaddition). The resultant C_s symmetry dimer structure (*o,p'*-dibenzene (**2**) tricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene) has the appearance of a 1,4-cyclohexadiene molecule bonded to a 1,3-cyclohexadiene molecule.

In addition to the equilibrium structure, four associated structures are determined; these are a stable C_1 symmetry biradical **3**, two C_1 symmetry transition states (TS) **4** and **5**, and a C_s symmetry "hill" **6**. The character of structures **1–6** was determined by examination of the Hessian matrix eigenvalues at these points. The TS's **4** and **5** lie on a reaction path in which the two new σ bonds form asynchronously; the stationary point **6** on a synchronous path leading from **1** to **2** corresponds to a hill rather than a TS. Diels–Alder reactions are usually assumed to occur along synchronous (concentrated) paths.

The structures **3**, **4**, and **5** are shown to have biradical character by both unrestricted Hartree–Fock (UMNDO) and 3 × 3 configuration interaction (CI) MNDO calculations; a biradical description for the other stationary points is less necessary.

The calculations allow one to give energy estimates of the magnitude of orbital symmetry effects for a specific set of cycloaddition reactions. The dimerization leading from **1** to **2**, along the asynchronous reaction path, has an activation barrier, at least, 40 kcal/mol less than those for the symmetry-forbidden dimerizations leading to **7**, **8**, **9**, and **10**, assuming the MNDO calculations are an adequate description.

Comparisons of the MNDO results with ab initio RHF and unrestricted Hartree–Fock (UHF) minimal basis set calculations and with group additivity results are made at the stationary points on the energy hypersurface.

There are indications that dimerization of aromatic rings, of which **2**, **7**, **8**, **9**, and **10** represent the simplest cases, plays an important role in the extreme high-pressure (ca. 10 GPa) behavior of aromatic materials (see ref 2a,b and references therein). The possible formation of **2** and **3** under such conditions is discussed.

The results of the present calculations are related to previous semiempirical and ab initio calculations of simpler D–A reactions, e.g., the ethene–butadiene reaction leading to cyclohexene. In particular, the question of whether the lowest energy reaction path leading from **1** to **2** is asynchronous is addressed.

The remainder of this paper is organized as follows. Section II gives the MNDO results for the species **1**, **2**, **3**, **4**, **5**, and **6**; in particular, their character (e.g., stable point or TS), geometry, and energy are presented. In Section III, comparisons are made between MNDO, minimal basis set ab initio, and group additivity energies at some of the stationary points in order to gauge the accuracy of the MNDO and UMNDO results. Section IV relates the present work to earlier work; the recent synthesis of **2** by other workers is also discussed.

II. Results at the Stationary Points

A. The MNDO Calculations. Most of the calculations to be reported used different forms of the MNDO[5] (modified neglect of diatomic differential overlap) method. This method gives semiempirical solutions of the Roothaan[6]–Hall[7] SCF-MO-LCAO equations. In the MNDO method, the computational requirements of the method are sharply reduced by (1) making the core approximation, (2) using a minimal basis set of valence shell atomic orbitals, and (3) only retaining integrals at the NDDO (neglect of diatomic differential overlap level).[8] The values of the remaining integrals are defined by a calibration to experimental data. The authors of the method indicate that this calibration mitigates errors due to use of the NDDO approximation and may also recover some of the correlation energy error associated with a single Slater determinant ab initio SCF theory. The greatest advantage of the MNDO method is that it makes feasible reasonably accurate computation of important characteristics (e.g., frequencies) of reaction surfaces of large structures with the use

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(1) This work was supported by the Department of Energy.

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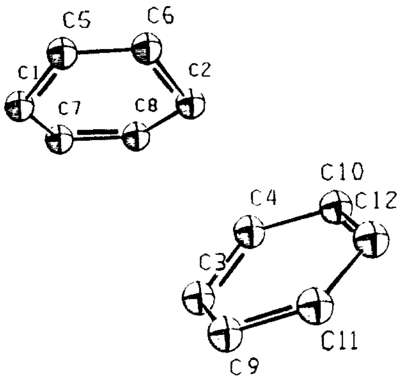

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Figure 1. Two separated benzene molecules **1** calculated with MNDO. This structure corresponds to the largest separation point on the asynchronous reaction path. C_1–C_3 and C_2–C_4 distances are 4.4 and 2.4 Å, respectively. At infinite ring separation, the RHF MNDO C–C benzene ring bond distance is 1.407 Å.

of acceptable amounts of computer time.

Accompanying these advantages are some deficiencies. Amongst these are the following: (1) it is not possible to systematically improve the theory because the approximations used in developing it are uncontrolled, (2) the calibration of the theory to experimental data involves macroscopic quantities (i.e., the temperature implicit in the heat of formation data); this is a deficiency in a theory purporting to be microscopic, and (3) when one attempts to improve the MNDO description (e.g., by doing a CI using the MNDO virtual orbitals), the question of including correlation effects twice must be faced. In spite of these difficulties, MNDO has been shown to be a useful procedure by extensive testing of it against experimental results (see, e.g., ref 9).

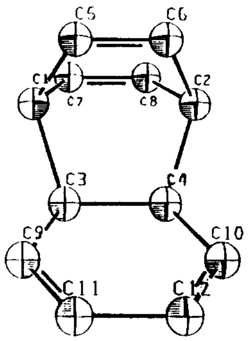
Since some of the structures to be considered contained unpaired electrons or electrons that are "unpairing", we also used the UMNDO method. This method is a semiempirical MNDO implementation of the UHF method first suggested by Pople and Nesbet.[10] UHF gives a useful single Slater determinant description of open shell systems. Details of UMNDO development, due to D. Landman, are apparently unpublished (see ref 11). The basic idea in the UHF formalism is that the space part of the spin-up and spin-down portions of a molecular orbital do not have to be identical. The resultant (UHF) Slater determinant is not an eigenfunction of the spin operator S^2.

Another method useful in describing singlet biradical-like species that was used involved a 3 × 3 CI wave function of the form

$$\Psi = \{c_1[|...\varphi_L\alpha\varphi_H\beta\rangle - |...\varphi_H\alpha\varphi_L\beta\rangle] + c_2|...\varphi_H\alpha\varphi_H\beta\rangle + c_3|...\varphi_L\alpha\varphi_L\beta\rangle\} \quad (1)$$

In the CI, HOMO and LUMO MNDO RHF orbitals are used; here these orbitals are denoted by φ_H and φ_L, respectively. The three dots (...) in eq 1 represent MNDO orbitals below the HOMO. Further description of this method can be found in the documentation of the MOPAC code.[4]

The geometries and energies of the structures **1**–**6** were obtained by using the RHF or UHF form of MNDO. The gradient minimization procedure employed to find the stable structures (i.e., structures for which all first space gradients of the energy are zero and all second space gradients are positive) used the Davidon–Fletcher–Powell algorithm.[12] When the stationary point being characterized had negative curvatures along some direction(s), the minimization was done on the gradient norm with Bartel's method.[13] The normal mode frequencies of the nuclei were used to characterize the stationary points. These frequencies were obtained by diagonalizing the Hessian matrix (the matrix of second derivatives of the energy with respect to displacements of all nuclear pairs). Zero or one negative frequency defines a



2

Figure 2. The stable C_s symmetry *o,p′*-dimer **2** calculated with MNDO. Representative C–C bond lengths (in Å) are C_1–C_5 = C_1–C_7 = C_3–C_7 = 1.57, C_5–C_6 = C_7–C_8 = C_9–C_{11} = 1.352, C_{11}–C_{12} = 1.462, and C_1–C_3 = C_3–C_4 = 1.58. Only the last two bond lengths are unusual. These bonds are strained due to the ring interconnection.

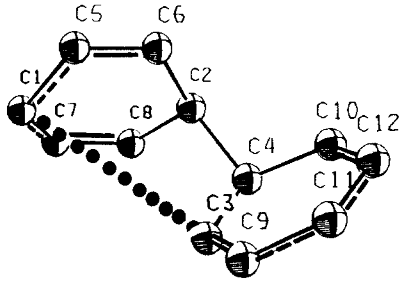


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Figure 3. The stable C_1 symmetry biradical **3** calculated with UMNDO. One σ bond has formed between the rings. Both rings resemble 1,4-cyclohexadiene. However, the bonds between carbons shown as -- resemble benzene ring π bonds more than σ bonds; they have lengths of 1.425 ± 0.001 Å. All the π bonds indicated by = are 1.396 ± 0.001 Å long; this value is close to that of an isolated benzene ring C–C bond. The intraring C–C bonds indicted by single lines (—) are all 1.512 ± 0.001 Å long; this value is significantly shorter than that of a standard sp^3 C–C bond. The substantially short C–C bonds in the portions of the ring away from the interring σ bond are indicative of additional electron population in these regions. The single σ bond connecting the rings is long, i.e., 1.579 Å. The C_1–C_3 distance is still very large, i.e., 3.608 Å; this distance in indicated by ●●●.

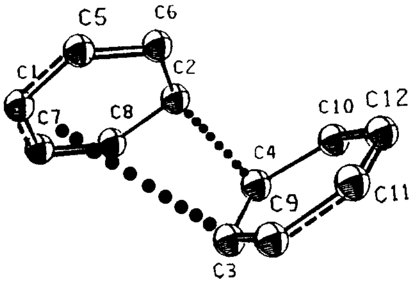

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Figure 4. The C_1 symmetry TS **4** calculated with UMNDO. All the "σ" bonds indicated by — are 1.460 ± 0.001 Å long; they are significantly shorter than standard sp^3 C–C bonds. The bonds indicated by -- are all 1.420 ± 0.001 Å long, which is reminiscent of the C–C bond distance in benzene, as are the bonds shown as =, which are all 1.406 ± 0.001 Å long. The interring distances C_1–C_3 and C_2–C_4 are 3.972 and 1.982 Å, respectively; these distances are indicated by the symbol ●●●.

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[9] (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907. (b) Thiel, W. *Ibid.* **1985**, *107*, 4422.

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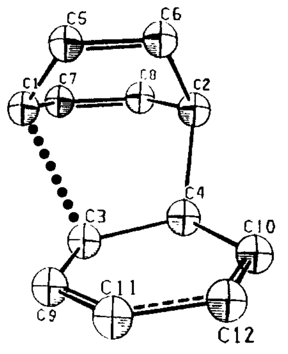

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Figure 5. The C_1 symmetry TS **5** calculated with UMNDO. Here, one interring σ bond has formed, and the second one is forming. The rings are beginning to resemble the cyclohexadiene structures they will have in the dimer **2**. The various C–C bond lengths (in Å) are (upper ring) C_1–C_5 = C_1–C_7 = 1.466 ± 0.002, C_5–C_6 = C_7–C_8 = 1.383 ± 0.002, and C_2–C_6 = C_2–C_8 = 1.518 ± 0.002 and (lower ring) C_3–C_4 = 1.536, C_9–C_{11} = C_{10}–C_{12} = 1.397 ± 0.007, C_3–C_9 = C_{11}–C_{12} = 1.438 ± 0.006, and C_4–C_{10} = 1.508. The C_1–C_3 and C_2–C_4 separations are 2.123 and 1.585 Å, respectively. The C_1–C_3 distance is indicated by ●●●.

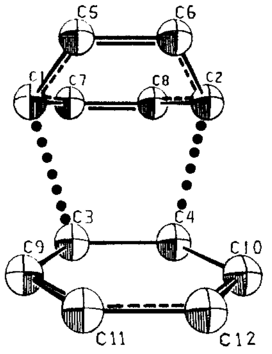

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Figure 6. The C_s symmetry "hill" **6** calculated with MNDO. The bonds represented by ═ have lengths 1.375 ± 0.003 Å; this is intermediate between an sp^2 π and a benzene ring C–C bond. Those bonds indicated by ╍ have lengths 1.447 ± 0.004 Å, while those designated by — are 1.458 ± 0.002 Å long. The intraring C–C bonds of this structure are less like those of benzene than those of **3**, **4**, and **5**. At the hill top, C_1–C_3 = C_2–C_4 = 2.094 Å; these distances are indicated by ●●●.

stable point or transition state, respectively. In MNDO, the first energy gradients are obtained analytically and the second space derivatives by numerical differencing.[14]

B. Stationary-Point Character and Geometries. The method used to find the optimum structures is given in the captions of Figures 1–6; important angles between carbon nuclei are given in Table I. Only the carbon nuclei positions are shown on the figures. The "error" bars given in the figure captions represent length differences between bonds of a particular type and not calculational errors. Full geometries of **1**–**6** are available from the author. The geometries, including hydrogen coordinates, were fully optimized within the indicated point groups.

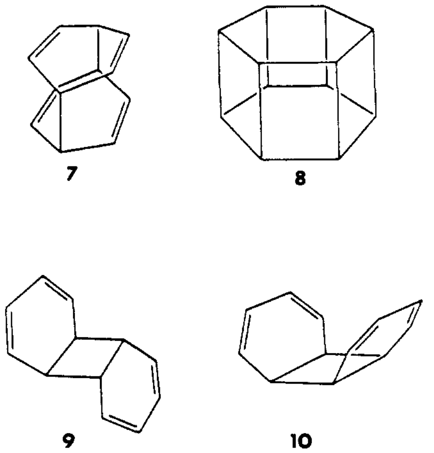
Note that **6**, which was expected to be the TS for a synchronous reaction mechanism, is a hill; it has two negative vibrational frequencies. This indicates the reaction takes place asynchronously, i.e., the two new σ bonds are formed sequentially.

When **6** was found to be a hill, the normal mode vectors associated with its two negative vibrational frequencies were used to define a structural distortion that allowed one to find the stable biradical **3**. The UMNDO wave function of **3** is nearly a pure triplet state; the value of $\langle S^2 \rangle$ at **3** is 2.089 measured in units of $\hbar^2$. Once **3** was found, reaction coordinate runs from **3** to **2** and from **3** to **1** gave the rough locations of **5** and **4**. Geometry optimizations were then made that gave the structures of **4** and **5**. Calculations of the normal vibrational frequencies at the optimized structures showed that both **4** and **5** are TS's.

Table I.[a] Carbon–Carbon Angles (deg)

	method[b]				
angle	2 MNDO	3 UMNDO	4 UMNDO	5 UMNDO	6 MNDO
C(1, 3, 5)	107.8	69.3	97.9	69.2	109.0
C(1, 3, 7)	106.5	73.0	96.3	71.8	85.3
C(1, 5, 7)	106.4	119.5	114.1	119.8	116.5
C(2, 4, 6)	107.8	112.5	108.5	108.8	109.0
C(2, 4, 8)	106.5	110.9	107.7	105.8	85.3
C(2, 6, 8)	106.4	111.6	108.1	116.0	116.5
C(3, 1, 9)	112.6	125.9	107.2	111.4	109.0
C(3, 4, 9)	115.1	123.0	119.7	121.2	118.0
C(3, 1, 4)	108.4	83.7	103.8	88.2	107.0
C(4, 2, 10)	112.6	111.7	111.9	105.9	109.0
C(4, 3, 10)	115.1	112.1	113.4	115.9	118.0
C(4, 2, 3)	108.4	113.4	111.1	108.7	107.0
C(5, 1, 6)	113.7	120.9	115.8	120.5	116.7
C(6, 2, 5)	113.7	122.4	115.4	121.2	116.7
C(7, 1, 8)	113.7	120.8	115.8	120.4	116.7
C(8, 2, 7)	113.7	122.5	115.3	121.3	116.7
C(9, 3, 11)	123.7	121.1	122.0	120.5	121.1
C(10, 4, 12)	123.7	123.0	123.0	121.3	121.1
C(11, 9, 12)	121.2	119.6	120.2	119.7	120.3
C(12, 10, 11)	121.2	121.1	121.1	120.4	120.3

[a] The point group of **2** and **6** is C_s and that of **3**, **4**, and **5** is C_1. [b] Method used to find the optimized structure.



7 **8** **9** **10**

Figure 7. The symmetry-forbidden dimer equilibrium structures. Only the carbon nuclei are shown.

Thus, provided MNDO is giving qualitatively correct information, the reaction **1** → **2** proceeds as follows: (1) At **4**, a single π bond in each ring is breaking, and a σ bond is incipient between the rings. The rings resemble 1,4-cyclohexadiene. The interring C–C distances (C_1–C_3 and C_2–C_4), where σ bonds will eventually form, are 3.972 and 1.982 Å. (2) At **3**, a stable biradical has formed. The first interring σ bond has appeared, and both rings of the biradical are still similar to 1,4-cyclohexadiene. The C_1–C_3 distance, where the second σ bond will eventually form, is 3.608 Å. (3) At **5**, the C_1–C_3 distance has been reduced to 2.123 Å; one ring resembles 1,4-cyclohexadiene and the other the 1,3-isomer. (4) At **2**, both interring σ bonds have formed. These σ bonds are about 0.05 Å longer than an unstrained C–C σ bond. The rings now closely resemble 1,3- and 1,4-cyclohexadiene. Structure **2** has only positive vibrational frequencies; i.e., it is stable.

It is of interest to examine the bond formation processes in more detail. At TS **4**, the C–C bond distances are still similar to those of benzene rings except those associated with C_2 and C_4. All the

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[14] Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135.

Table II. Stationary Point Relative Energies (kcal/mol)[a]

method	1	2	3	4	5	6
MNDO	0.0	31.1	74.1	55.9	71.7	83.6
UMNDO	0.0	27.9	18.7	34.7	55.0	73.3
(U)MNDO-ZPC[b]	0.0	41.1	17.7	31.7	55.0	86.8
MNDO-Birad	0.0	29.8	49.1	56.7	73.7	84.8
ab initio(RHF)[c,d]	0.0	7.6	119.4	68.4	73.3	110.4
ab initio(UHF)[c,d]	0.0	24.3	21.4	30.4	45.4	89.1
group additivity	0.0	25.8	(55?)		(55?)	

[a] Energies are relative to two benzenes calculated by the same method. [b] MNDO or UMNDO energy corrected for zero point vibrations. [c] These results were obtained with the Gaussian-82 code by using the MNDO or UMNDO optimized geometries. The Gaussian-82 code is due to J. Pople and his coworkers, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213. [d] The UHF(RHF) ab initio absolute energy for benzene at the MNDO optimized coordinates is −455.78636 (−455.76444) hartrees.

Table III. Sum of Zero-Point Frequencies (kcal/mol)[a]

structure	sum	no. of modes	method[b]
1	263 (0.0)[c]	60	MNDO
2	273 (10.0)	66	MNDO
3	262 (−1.0)	66	UMNDO
4	263 (0.0)	65	UMNDO
5	260 (−3.0)	65	UMNDO
6	266 (3.0)	64	MNDO

[a] The negative frequencies for **4**, **5**, and **6** are not included in the sums. [b] Method used to obtain the frequencies. [c] Values in parentheses are the zero-point corrections relative to two benzenes.

Table IV. Squares of Configuration Interaction Coefficients[a]

structure	c_1^2	c_2^2	c_3^2
1	0.0	0.980	0.020
2	0.0	0.964	0.037
3	0.0	0.805	0.195
4	0.0	0.926	0.074
5	0.0	0.946	0.054
6	0.0	0.980	0.020

[a] See eq 1 of the text for the configurations corresponding to the c_i's.

intraring C–C bond angles are within about 4° of their benzene ring values. The incipient σ bond is 0.45 Å longer than its final value in **2**. TS **4** strongly resembles the stable biradical **3**; all angles in Table I for **3** and **4** are the same within about 6° except C(3, 1, 9). The major changes in going from **4** to **3** are the C–C bond distances associated with C_2 and C_4. Going from **3** to TS **5** causes stronger changes. The most important of these being in the C–C distances of C_1 and C_3 and the switch of the lower ring toward a 1,3-cyclohexadiene form from what had looked like the 1,4-isomer. The C_1–C_3 distance has been reduced to 2.12 Å. TS **5** is more like **2** than **3**. In going from **5** to **2**, all the C–C bond lengths relax significantly to values close to those of normal C–C σ and (conjugated and unconjugated) π bonds. At **2** only the C–C bonds C_1–C_3 and C_2–C_4 deviate significantly (by about 0.05 Å) from normal bond lengths; some bond angles of carbons 3, 4, 5, 6, 7, and 8 deviate from normal by more than 5°. These deviations are due to strain imposed by the interring bonds.

One can summarize the CH bonding by noting that the only unusual bonds occur on the carbons that take part in the new interring σ bonds; i.e., C_2 and C_4 on **3**, **4**, and **5** and C_1 to C_4 on **2** and **6**. The CH bonds that differ significantly from normal (i.e., which are different from 1.090 Å by more than 0.007 Å) are all long. The extreme cases occur on **2**, **3**, and **5**, where they are larger than normal by roughly 0.04 A.

Fully optimized geometries and energies along reaction paths $\mathbf{1} \rightarrow \mathbf{4} \rightarrow \mathbf{3} \rightarrow \mathbf{5} \rightarrow \mathbf{2}$ and $\mathbf{1} \rightarrow \mathbf{6} \rightarrow \mathbf{2}$ have been calculated and are available from the author.

C. Stationary Point Energies. Next the energies of **1–6** are compared. Since **3**, **4**, and **5** are structures with unpaired electrons or in which bonds are forming, their geometries were obtained with UMNDO. The geometries of **1**, **2**, and **6** were obtained with MNDO. The RHF and UHF MNDO energies calculated at the optimized geometries are given in Table II. The UMNDO energies should be taken as superior. For **1** and **2**, the MNDO and UMNDO results agree to 3.2 kcal/mol or better. For two isolated benzenes, UMNDO gives a heat of formation 1.8 kcal/mol greater than MNDO, if the MNDO geometry is used. For the hill **6**, there is agreement to about 10 kcal/mol. However, for **3**, **4**, and **5**, where electron unpairing is suspected, UMNDO gives energies significantly lower than MNDO. For example, the energy difference between the RHF and UHF results for **3** is greater than 55 kcal/mol.

Since frequencies were calculated to determine the character of **1–6**, it is possible to correct the relative energies for zero-point vibrational effects. The zero-point corrected relative energies are given in row 3 in Table II. The zero-point corrections (ZPC) can be significant; e.g., the energy of metastable **2** is raised by 10 kcal/mol, relative to two benzenes, by the ZPC. Note that making ZPC within the MNDO/UMNDO framework is ambiguous as the empirical calibration of these methods to experimental free energies probably introduces some ZPC effects. The sum of the ZP frequencies for each structure is given in Table III, along with other pertinent data. Assuming the ZP corrected energies are the most accurate, the following can be concluded: (1) the stable forms **2** and **3** are metastable relative to two benzenes by 41.1 and 17.7 kcal/mol, respectively, (2) the TS energies that need to be surmounted to reach **3** and **2**, from two benzenes, are 31.7 (TS **4**) and 55.0 (TS **5**) kcal/mol, respectively, and (3) the hill **6** lies much higher in energy (>30 kcal/mol) than the TS **5** by which **2** is reached from **1**. The large energy difference between **6** and **5** indicates that the mechanism of the reaction leading from **1** to **2** is probably asynchronous; i.e., the same conclusion would be reached even with more rigorous calculational methods. This question will be considered further below. The normal mode vectors and vibrational frequencies for all the structures are available from the author.

Finally, consider the energies (Table II) obtained with the 3 × 3 CI ("biradical") MNDO wave function, eq 1. For **2**, **4**, **5**, and **6**, the 3 × 3 CI energies agree with the MNDO results to within about 2 kcal/mol; for **3** (the "biradical" stable point), the 3 × 3 CI produces a significantly lower energy than MNDO (about 25 kcal/mol). Table IV gives the squares of the CI coefficients. One sees that c_1^2 (the coefficient for the antisymmetric combination of the one-electron excitations term squared) is negligible, c_2^2 (the MNDO ground state coefficient squared) is large, i.e., >0.80 and c_3^2 (the HOMO–LUMO double excitation term squared) varies from small to moderately large. c_3^2 is only greater than 0.05 for **3**, **4**, and **5**, indicating biradical character for these structures. The double excitation accounts for roughly 20% of the probability density in the stable biradical **3** CI wave function. These results are in agreement with intuition concerning the character of **1–6**. The UMNDO energies are markedly lower (about 18 kcal/mol) than the 3 × 3 CI energies for **3**, **4**, and **5**. The UMNDO energies have been taken as superior to the biradical energies principally because there has been greater published testing of UMNDO results against experiment.

III. Comparisons of Energies Obtained with Different Methods

The purpose of this section is to strengthen the credibility of the UMNDO and MNDO results by comparison with results derived with other methods (i.e., ab initio and group additivity energies). The ab initio energies were obtained with the Gaussian-82 code at the (U) MNDO geometries. Both RHF and UHF calculations used a minimal (STO-3G) basis set. In the UHF calculations the equivalence of the spin-up/spin-down space orbitals was broken by an initial mixing of the HOMO and LUMO RHF orbitals. The group additivity energies were obtained by using the method described by Benson.[15] All the energies are collected in Table II.

The comparisons can be usefully broken into two cases. First, for the stable dimer structure **2**, the MNDO, UMNDO,

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(15) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; Chapter 2.

MNDO-birad, ab initio UHF, and group additivity methods all agree to within 7 kcal/mol. This is important because the group additivity value for this stable structure is probably quite accurate. The ab initio UHF(STO-3G) value agrees well with it, giving some confidence in the ab initio UHF method for this type of structure. Most importantly, the much simplified UMNDO method agrees well with the ab initio UHF result, indicating that the approximations used in obtaining UMNDO from the ab initio UHF equations have not ruined its accuracy. The RHF(STO-3G) ab initio results are further off, probably due to the inabilities of such calculations in describing small strained rings.

Second, for the structures **3**, **4**, **5**, and **6**, in which some electrons are more or less unpaired, and in which one expects an ab initio UHF method to give an adequate description, continued good agreement (generally to with 10 kcal/mol or less) is found between the ab initio UHF and the computationally much simpler UMNDO method. This strengthens one's faith in the accuracy of the UMNDO results. It is important to realize that it would be currently computationally unreasonable to attempt the UMNDO calculations presented here (e.g., geometry optimizations and stationary point characterizations of a $(CH)_{12}$ structure) with an ab initio UHF method. As expected, the ab initio RHF energies for **3**, **4**, **5**, and **6** are much larger than the ab initio UHF and UMNDO results, indicating the effectiveness of unrestricted HF methods in systems where electron unpairings are occurring.

These observations support the idea that the UHF ab initio and UMNDO energy hypersurfaces approximately parallel one another. This strengthens the idea that the UMNDO optimized geometries and energies are acceptable estimates.

One further comment is that it was also possible to estimate the group additivity energy of the radical cyclohexadien-1,4-yl-6. The energy of this structure relative to benzene is found to be 55 kcal/mol. This energy does not agree well with the UMNDO value for **3**. In a group additivity analysis, it is implicit that bond lengths and angles are those corresponding to an ordinary hybridization of the atomic orbitals. The geometry given above for **3** shows this is not true of **3**. Note, however, that the bond lengths and angles of **5** are tending toward those of two normal cyclohexadiene molecules. Perhaps this observation helps explain the agreement of the UMNDO energy for **5** and the group additivity energy for **3**. Group additivity energies are not given for **4** and **6** because the method can only be applied to hypersurface minima, at present.

IV. Summary

Numerous workers (see, e.g., ref 16 and 17) have theoretically studied the simplest [4 + 2] cycloaddition—the ethene–butadiene D–A reaction. Interestingly, the best semiempirical (MNDO and MINDO/3) and ab initio (RHF/STO-3G/full gradient optimization) calculations, to date, disagree qualitatively on the reaction mechanism, predicting asynchronous and synchronous mechanisms, respectively. Sauer and Sustmann[18] give a thorough review of experimental and theoretical work on the D–A reaction mechanism to 1980. They point out that interpretation of all D–A reactions in terms of a single mechanism may be an intrinsically flawed idea. However, this does not relieve the difficulty of disagreement of methods on a single reaction. McIver[19] used group theoretical arguments, supported by assumptions concerning the relative values of force constants at a C_s symmetry D–A "TS", to show that such a TS is unlikely. However, the ab initio calculations of Brown and Houk[17b] of the butadiene–ethene D–A reaction show that McIver's arguments are not valid, at least, at the STO-3G basis set level. They showed that there is a C_s TS on the STO-3G energy hypersurface by computing all the normal mode vibrational frequencies and finding only one negative value at a C_s symmetry stationary point. It has been shown that ab initio STO-3G post HF calculations (second- and third-order Møller–Plesset perturbation theory) tend to bring the RHF ab initio energy surface toward the MNDO one, in the vicinity of the ab initio synchronous TS.[20] This raises the question of whether the conclusions on reaction mechanism are sensitive to inclusion of correlation energy effects. Whether the asynchronous or synchronous mechanism (or a combination of them) is in effect in the ethene–butadiene reaction is still open. The benzene dimerization results presented here agree with earlier semiempirical calculations on the ethene–butadiene reaction; i.e., the reaction mechanism is predicted to be asynchronous. The large differences in the UMNDO-ZPC energies for points **5** and **6** (see Table II) would seem to be outside the energy errors normally associated with the (U)MNDO method. It would clearly be desirable to do a high quality ab initio MCSCF calculation on the ethene–butadiene reaction to try to resolve the important question of the reaction mechanism of the simplest D–A reaction.

One can compare the energies associated with orbital symmetry effects in cycloadditions by use of the results in Table II and ref 2a. The reactions of interest are **1** → **2** (a [4 + 2] symmetry-allowed cycloaddition) and **1** → **7** (a [4 + 4] symmetry-forbidden cycloaddition). The two points on the $C_{12}H_{12}$ energy hypersurface considered correspond to D_{2h} and C_s modes of approach of the two benzenes (leading to products **7** and **2**, respectively). For the symmetry-allowed reaction the barrier point of interest is **6** with an MNDO energy of 83.6 kcal/mol relative to two benzenes. The MNDO energy for the analogous point for **7** is 127 kcal/mol (see ref 2a). Thus, the energy increase associated with the symmetry-forbidden path and its consequent orbital crossing is about 43 kcal/mol.

It is possible that **2** and **3** are formed by application of extreme pressure (ca. 13.3 GPa) to benzene. In ref 2b, the formation of structure **7** under such conditions was examined. It was found that essentially all the energy delivered by the 13.3 GPa shock (necessary to produce the onset of the observed rate process in benzene) was required to surmount the calculated 127 kcal/mol MNDO barrier leading to **7**. For this to be feasible, required an assumption of an extreme lack of thermodynamic equilibrium immediately behind the shock wave. The much smaller energies required to form **3** (31.7 kcal/mol) and **2** (55.0 kcal/mol) reduce the need for this assumption. Only about one-fourth the energy delivered by the 13.3 GPa shock would bring all the molecules to TS **4**.

Finally, there is recent experimental evidence of the actual synthesis of **2**.[21] The activation barrier for the retro D–A reaction **2** → **1** is found experimentally to be 14.7 ± 0.4 kcal/mol (error bar = 2 standard deviations). This experimental result agrees satisfactorily with the UMNDO-ZPC activation barrier for the retro reaction **2** → **5** of 13.9 kcal/mol. The retro reaction **3** → **4** also has nearly the same calculated barrier (14.0 kcal/mol). It is also of note that the dimers analogous to **2** of the form (benzene-2nd arene) have also been experimentally isolated, when the 2nd arene is naphthalene or anthracene.[22a,b] The activation barriers to formation of these structures are 19.5 and 24.9 kcal/mol, respectively.

Registry No. C_6H_6, 71-43-2.

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