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Electrocyclic Ring Opening Modes of Dewar Benzenes: Ab Initio Predictions for Möbius Benzene and *trans*-Dewar Benzene as New C_6H_6 Isomers

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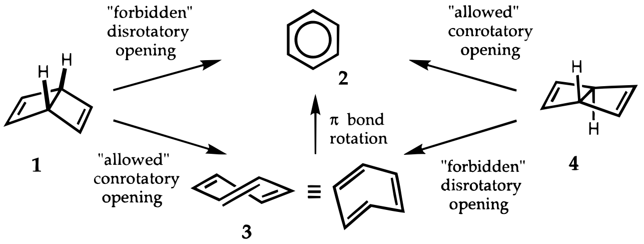
Abstract: Ab initio calculations have been performed on the two modes of electrocyclic ring opening of Dewar benzene (**1**), as well as related structures. Both CASSCF and MP2 optimizations predict the existence of Möbius benzene (**3**, *cis*,*cis*,*trans*-1,3,5-cyclohexatriene) in a very shallow minimum ca. 100 kcal/mol above benzene (**2**). This structure has alternating single and double bonds, with one fully trans double bond. The barrier for π bond rotation (**3** → **2**) is predicted to be less than 3 kcal/mol. Stationary points have been located at the TCSCF/6-31G* level for both conrotatory and disrotatory ring opening of **1**. The disrotatory path proceeds through a second-order saddle point, which appears to be a general characteristic of symmetry-forbidden reactions. At every level of calculation, conrotatory ring opening of **1** proceeds through a barrier that is 1.5−5.1 kcal/mol lower than disrotation. The predicted conrotatory enthalpic barrier of 24−28 kcal/mol agrees well with the experimental value of 25.1 ± 2. Intrinsic reaction cordinate calculations suggest that conrotation from **1** may lead to either **2** or **3**. Calculations also support the existence of *trans*-Dewar benzene (**4**), a substance originally suggested by Woodward and Hoffmann in 1971. This is predicted to be 158 kcal/mol above benzene, but still has a barrier of ca. 13 kcal/mol for ring opening to benzene.

Introduction

Benzene chemistry is rich with high-energy structures that interconvert through complex and mysterious rearrangements.[1−3] In spite of the long history of this field, new and fascinating benzene isomers still are being discovered.[4] The synthesis of Dewar benzene (**1**) was reported in 1962 by van Tamelen and Pappas.[5] Wilzbach and co-workers later showed that **1** also is a product of benzene photochemistry.[6] Much attention has been devoted to the mechanism for ring opening of **1** to benzene (Scheme 1), which often is cited as a textbook example[7,8] of an orbital symmetry controlled process.[9] Although several complex mechanisms were originally considered[9] for ring opening of **1** to **2**, deuterium-labeling studies by Goldstein and Leight[10] provided evidence for straightforward σ bond cleavage, without measurable scrambling of ring atoms. The enthalpic barrier for ring opening has been shown to be 23−25 kcal/mol.[11,12] As one consequence of the high reaction exothermicity, Turro and co-workers found that isomerization of **1** leads to production of a modest amount of triplet excited state benzene.[12] The expected stereochemical mode for ring opening was clearly defined by van Tamelen:[5] “In the case of Dewar benzene, this preferred thermal mode of ring opening (conrotatory) cannot operate since an extraordinarily strained *cis*,*cis*,*trans*-cyclohexa-1,3,5-triene would result.” This led to the universal assumption that ring opening of Dewar benzene must follow an orbital symmetry forbidden disrotatory path.

Scheme 1. Potential Electrocyclic Pathways for Dewar Benzenes



[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1996.

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Table 1. Results of Ab Initio Calculations on Möbius Benzene (**3**)

	benzene (D_{6h})	π bond rotation transition state (C_2)	Möbius benzene (C_2)
CASSCF(6,6)/3-21G	−229.494191 (0.0)[a]	−229.332313 (101.6)	−229.337325 (98.4)
CASSCF(6,6)/6-31G*[b]		−230.616051	−230.620750
ZPVE[b]	66.5	62.3	64.1
entropy[b,d]	63.4	69.3	68.6
MP2/6-31G*	−231.457734 (0.0)		−231.288904 (105.9)
MP4SDTQ/6-31G* [c]	−231.531856 (0.0)		−231.371106 (100.9)
ZPVE[c]	63.2		61.3
entropy[c,d]	64.7		71.6
Becke3LYP/DN* [c,e]	−232.195223 (0.0)		−232.037949 (98.7)
BP86/DN* [c,e]	−232.305933 (0.0)		−232.149435 (98.2)

[a] Energies relative to benzene are given in parentheses. [b] CASSCF (6,6)/3-21G optimized geometry. [c] MP2/6-31G* optimized geometry. [d] cal mol^{-1} K^{-1}. [e] Calculations with Spartan, Version 4.04.[17]

In principle, there might exist a complementary structure, *trans*-Dewar benzene (**4**). Because of the trans-fused ring juncture, conrotatory ring opening is expected to be highly favored for **4**. In their seminal treatise on orbital symmetry, Woodward and Hoffmann proposed the existence of this novel molecule, and further issued a challenge to determine its lifetime.[9] The only reported study on **4** is due to Dewar and co-workers, who used the MNDO method to predict that this substance will rest in an energy minimum with a barrier of 5.0 kcal/mol for conrotatory ring opening to benzene.[13] Symmetry forbidden disrotatory opening of **4** should yield **3**.

We report here the results of ab initio investigations on the chemistry outlined in Scheme 1. Our results include the first prediction that C_6H_6 isomer **3**, sometimes referred to as "Möbius benzene", should exist in a shallow energy minimum. We also provide further support for the potential existence of **4**. Perhaps our most surprising conclusion is that *conrotatory* ring opening provides the lowest energy pathway from **1** to **2**.

Results and Discussion

Does *cis*,*cis*,*trans*-1,3,5-Cyclohexatriene (3) Exist? Both experiment and theory have provided convincing evidence for the existence of *trans*-cyclohexene.[14,15] Because of the obvious structural similarity, we investigated the existence of **3**. As noted above, this strained C_6H_6 valence isomer appears to have been first considered by van Tamelen as an unlikely product from conrotatory opening of **1**.[5] In 1966, Farenhorst proposed "Möbius benzene" as a photoproduct of benzene, and precursor to other valence isomers.[16a] Bryce−Smith and Gilbert have suggested that Möbius benzene (**3**) might result from S_2 of benzene, and thus provide a route to benzvalene.[2] Mulder suggested that Möbius benzene should correspond to a minimum in S_1.[16b] *cis*,*cis*,*trans*-1,3,5-Cyclohexatriene might be exceedingly difficult to detect by experiment, but theory should provide a reliable verdict on its existence.

The energy-minimized structure for **3** proved surprisingly easy to locate. Geometry optimization with Hartree−Fock, MCSCF, or MP2 wave functions[17−19] all led to a remarkable structure with C_2 symmetry and a trans bond H−C═C−H dihedral angle close to 180°. Previous studies on *trans*-cyclohexene have shown that a TCSCF (two-configuration SCF) wave function adequately models both the strained π bond and the rotational barrier.[15] In the case of **3**, the more extended π system required expansion of the active configurational space to six orbitals and six electrons. Optimization in C_2 symmetry with a CASSCF-(6,6)/3-21G wave function[18] was followed by single-point CASSCF(6,6)/6-31G* calculation. To confirm that this result was not an artifact of the CASSCF methodology, MP2/6-31G* optimization[19] was carried out, with the application of stringent convergence criteria. In each case, Hessian calculation proved that the optimized structures were true minima. To provide the most accurate energetic comparisons, single-point calculations were then carried out at the MP4 level and with several density functional methods.[17] Total energies and other data are summarized in Table 1, while Figure 1 shows the optimized structure. The trans π bond in **3** is substantially pyramidalized, as was previously observed with *trans*-cyclohexene,[14] and the structure shows localized π bonds.

The transition state for π bond rotation also was located with a CASSCF(6,6)/3-21G wave function, which is expected to accurately describe its diradical character. Numeric CASSCF Hessian calculation on this optimized structure (Figure 2) resulted in a single imaginary frequency (−725.6 cm^{-1}); animation with MacMolPlt[20] confirmed that this normal mode corresponded to π bond rotation. As expected for this highly strained structure, the CASSCF rotational barrier is much smaller than that for *trans*-cyclohexene.[15] For **3**, the difference in CASSCF(6,6)/6-31G* total energies gives a barrier of 2.95 kcal/mol. With correction for zero-point differences, this barrier is diminished to only 1.09 kcal/mol; factoring in entropy gives $\Delta G^{\ddagger} = 0.91$ kcal/mol. Clearly, this structure represents a shallow energy minimum; at some higher levels of theory, no minimum may exist for **3**.

Incorporation of a trans double bond in benzene thus yields a highly strained structure, ca. 100 kcal/mol above the D_{6h} global

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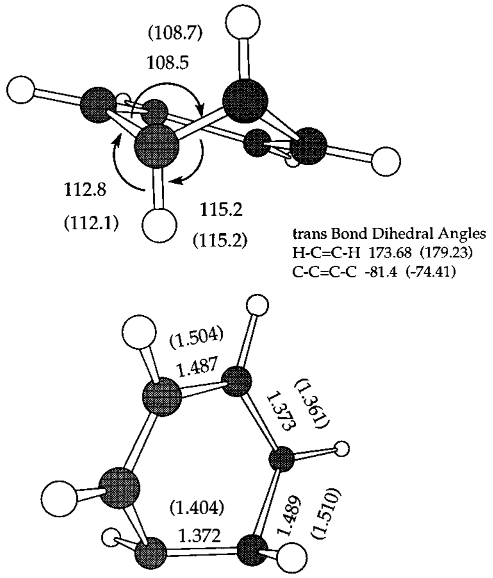

Figure 1. MP2/6-31G* and (in parentheses) CASSCF(6,6)/3-21G optimized geometries for Möbius benzene (**3**).

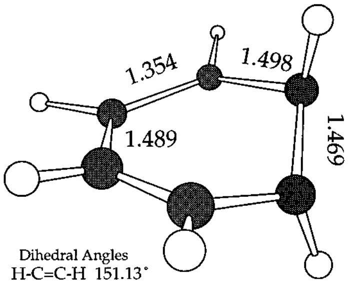

Figure 2. CASSCF(6,6)/3-21G optimized geometry for the Möbius benzene (**3**) π bond rotation transition state.

Table 2. Results of Calculations on Dewar Benzene (**1**)

	Dewar benzene (C_{2v})	conrotatory transition state (C_s)	disrotatory saddle point (C_{2v})[c]
TCSCF/3-21G		−229.254428	−229.251994
TCSCF/6-31G*		−230.540618	−230.537837
ZPVE[b]		63.50	62.11
entropy[b]		69.25	68.16
MP2/6-31G*	−231.329561	−231.282056	*d*
MP4SDTQ/6-31G* [a]	−231.406142	−231.359264	
MP4SDTQ/6-31G* [b]		−231.351732	−231.343591
ZPVE[a]	62.02	60.58	
entropy[a]	67.93	69.31	
Becke3LYP/DN* [a,e]	−232.059521	−232.021572	
BP86/DN* [a,e]	−232.178674	−232.137552	

[a] MP2/6-31G* geometry. [b] TCSCF/6-31G* geometry.. [c] Second-order saddle point. [d] Structure search unsuccessful at this level. [e] Calculations with Spartan, Version 4.04.[17]

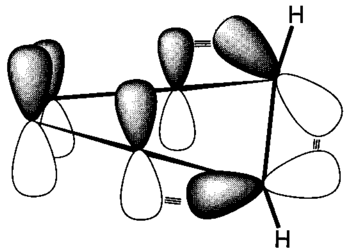

Figure 3. Möbius basis orbital array in **3**.

minimum and with a very small barrier for isomerization. Strain in *trans*-cyclohexene has been estimated at ca. 55 kcal/mol.[15] In **3**, the ring constraints are certainly more severe and the structure has lost the stabilization of ca. 40 kcal/mol associated with aromaticity. Thus, the energy of this species relative to benzene is about as expected.

We can only speculate on the relationship of this work to benzene photochemistry. Simple π bond isomerization is a ubiquitous reaction of alkene excited states and it is possible that trans isomer **3** is one primary benzene photoproduct. However, because of the low barrier predicted for π bond rotation, **3** seems an unlikely precursor to other benzene valence isomers. Direct conversion of **3** to benzvalene might be viewed as an intramolecular $[{}_{\pi}2_{s} + {}_{\pi}4_{a}]$ process, which would be symmetry forbidden. Although **3** has been suggested[2] as arising from benzene S_2, detailed studies of benzene excited state pathways do not seem to have considered this reaction mode.[21]

Is the structure in Figure 1 "Möbius benzene" as previously suggested?[2,5,16] Heilbronner first described the fascinating topology of the Möbius annulene series.[22] Zimmerman later expanded this concept in the construction of a set of rules for pericyclic reactions[23] that are complementary to those defined by Woodward and Hoffmann.[9] The optimized geometry for **3** at each level (Figure 1) does not have the idealized Möbius topology envisioned by Heilbronner. However, as shown in Figure 3, the π orbital basis does describe a Möbius array. Möbius benzene would be antiaromatic, but we expect this plays a negligible role in destabilizing **3**. Because of previous usage, and the existence of a Möbius basis orbital topology, we support calling this structure Möbius benzene.

Electrocyclic Ring Opening of Dewar Benzene. If **3** exists, albeit in a shallow minimum, the next logical question is whether it could be on the pathway for ring opening of Dewar benzene (**1**).[13,24] The MP2/6-31G* optimized structure for **1** is shown in Figure 4.[25] At the MP4//MP2(+ZPVE) level, this substance is predicted to be 77.8 kcal/mol above benzene, and only ca. 21.2 kcal/mol below **3**. The conrotatory transition state connecting **1** and **3** was readily located at the HF, TCSCF, or MP2 levels of theory. Figure 5 shows the saddle-point structure, as well as TCSCF normal mode vectors that clearly correspond to conrotation upon cleavage of the σ bond. To ensure this is the correct path, the HF/3-21G and TCSCF/3-21G intrinsic reaction coordinates were calculated with GAMESS[17] in both directions from the transition state. In one direction on the HF/3-21G intrinsic coordinate, this led smoothly back to **1**; in the other, the structure maintained a symmetry plane until about halfway, then reached a bifurcation point where it broke symmetry to localize the double bonds in one enantiomer of **3**. On the TCSCF/3-21G intrinsic coordinate, the structure continued down from this point toward benzene, rather than falling into the shallow minimum for **3**. The dynamics at this critical point probably are quite dependent on the level of calculation, but present results suggest that beyond the conrotatory transition state, the structure may either give **3** or go directly to benzene.

The MP4//MP2 enthalpic barrier (corrected for ZPVE differences) is 28.0 kcal/mol, which is slightly higher than the best

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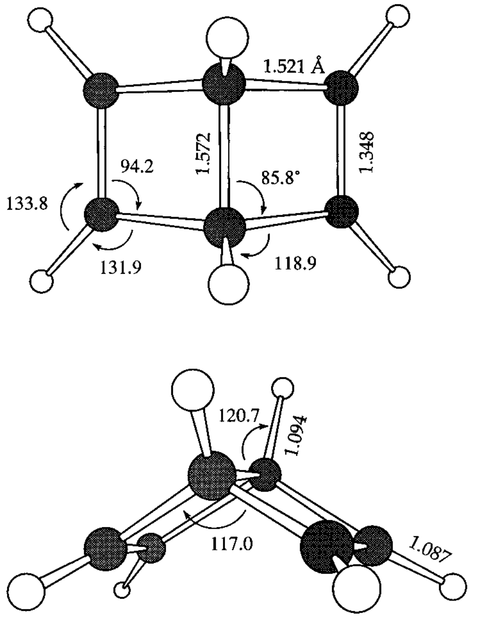

Figure 4. MP2/6-31G* optimized geometry for Dewar benzene (**1**).

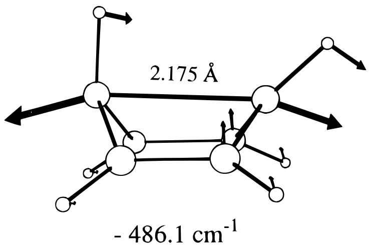

Figure 5. Conrotatory reaction saddle point normal mode from TCSCF/6-31G* calculation.

experimental value of 25.1 ± 2 kcal/mol.[12] Our predicted $\Delta G^{\ddagger}$ is 27.6 kcal/mol. Selected density functional calculations[17] at the MP2/6-31G* optimized geometries afforded barriers of 25.8 (BP86/DN*) and 23.8 (Becke3LYP/DN*) kcal/mol, in good agreement with the MP4 predictions.

Earlier theoretical studies on this reaction appear to have universally assumed a disrotatory pathway.[13,24] In the most complete MNDO study, Dewar, Ford, and Rzepa obviously found the conrotatory transition state, which is shown as one structure in this paper.[13] However, because they believed this to be impossible, this result was ascribed as an "error"!

Calculations on the orbital symmetry forbidden disrotatory path were restricted to the requisite 4-fold (C_{2v}) symmetry. Because a symmetry-forbidden reaction requires an orbital crossing, the best wave function includes at least two configurations.[26,27] A true stationary point was successfully located with a TCSCF/6-31G* wave function, but Hessian calculation resulted in two imaginary frequencies, thus characterizing this as an unusual second-order saddle point. Similar observations of second-order saddle points have been made for the disrotatory opening of cyclobutene[27a] and the [$_{\pi}2_s + {}_{\pi}2_s$] dimerization of ethylene.[27b,c] Thus, it appears this may be the general case for orbital symmetry forbidden reactions. Figure 6 shows the two normal modes. The larger mode corresponds to ring opening, while the smaller mode describes distortion back to the lower energy conrotatory path, which represents the true transition state. Intrinsic reaction coordinate calculation led smoothly from the C_{2v} saddle point toward either reactant or product. Attempts to locate a second-order saddle point for the disrotatory path at the MP2/6-31G* level with GAUSSIAN were not successful.

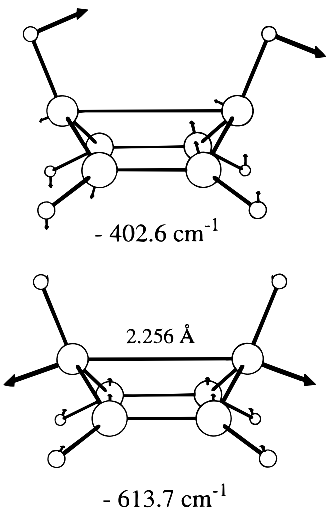

Figure 6. Disrotatory reaction second-order saddle point normal modes from TCSCF/6-31G* calculation.

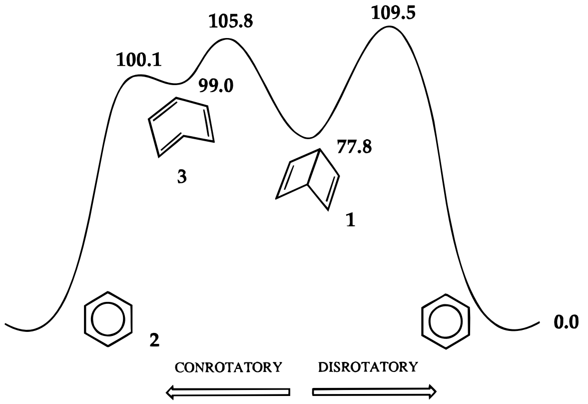

Figure 7. Potential energy diagram (kcal/mol) for conrotatory and disrotatory opening of Dewar benzene.

Higher level single-point calculations were carried out to more accurately assess the relative energies of the C_s and C_{2v} stationary point structures at the TCSCF/6-31G* optimized geometries. In every case, the conrotatory mode was slightly lower. Predicted total energy differences (kcal/mol) for the two modes include the following: TCSCF/6-31G* 1.75; MP4SDTQ/6-31G* 5.11; BP86/DN* 3.46; Becke3LYP/DN* 2.67; and SVWN/DN* 4.66. Zero-point differences would diminish these values by 1.4 kcal/mol.

Figure 7 summarizes our best estimates of the relative enthalpies for all of these species. Most data are from MP4 energies. While it is possible that some other mode of lower symmetry exists, the present results are consistent with *conrotation* as the lowest energy path for ring opening of **1**. The reaction energetics permit formation of valence isomer **3**, which would undergo nearly instantaneous π bond rotation to benzene.

Our predicted barrier is in reasonably good agreement with experiment, but does not unambiguously define the reaction mode since the disrotatory path is only slightly higher. No stereochemical features of the benzene structure permit correlation with experiment. Because the disrotatory and conrotatory transition states have very different shapes, they would be expected to define different activation volumes ($\Delta V^{\ddagger}$).

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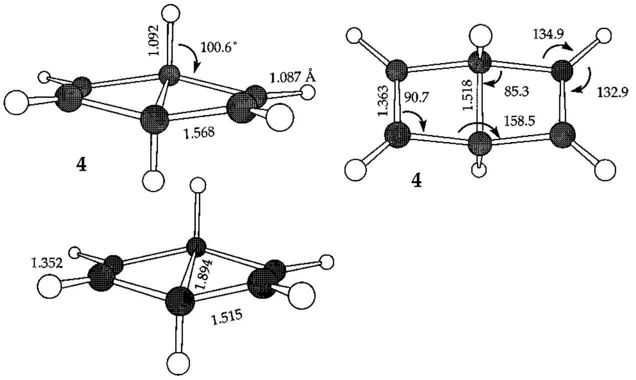

Figure 8. MP2/6-31G* optimized geometries for *trans*-Dewar benzene (**4**) and the transition state for its conrotatory ring opening.

Table 3. Results of Ab Initio Calculations on *trans*-Dewar Benzene (**4**)[a]

	trans-Dewar benzene (C_{2h})	conrotatory transition state (C_{2h})
MP2(FC)/6-31G*	−231.19956 (162.3)	−231.174745 (177.6)
MP4SDTQ/6-31G*[b]	−231.279891 (158.1)	−231.255601 (173.4)
ZPVE	61.4	59.3
entropy[c]	68.4	70.0
Becke3LYP/DN*[b]	−231.939444 (160.5)	−231.919916 (172.8)
BP86/DN*[b]	−232.059276 (154.8)	−232.036629 (169.0)

[a] Energies relative to benzene are given in parentheses. [b] MP2(FC)/6-31G* optimized geometry. [c] cal mol^{-1} K^{-1}.

LeNoble has measured $\Delta V^{\ddagger} = 5.0 \pm 2$ cm^3/mol for ring opening of **1**.[28] Methods for simulating activation volumes are being developed[29] and may eventually provide correlation with our results.

Existence and Ring-Opening Modes for *trans*-Dewar Benzene (4). Structure **4** (Scheme 1) has been called *trans*-Dewar benzene.[13] Optimizations at the HF/3-21G or MP2/6-31G* levels readily located both an energy minimum for this structure and the transition state for its conrotatory ring opening to benzene. In each case, Hessian calculation confirmed the nature of the stationary point. Single-point MP4 and density functional calculations were carried out to more accurately assess energetics relative to benzene. The optimized structures, which both possess C_{2h} symmetry, are shown in Figure 8; energies are collected in Table 3. By comparison to benzene, structure **4** lacks aromaticity, and contains two trans-fused four-membered rings as strain elements. Not surprisingly, this substance is predicted to be ca. 158 kcal/mol (!) above benzene. For the ring opening, our best estimates are $\Delta H^{\ddagger} = 15.0$ kcal/mol and $\Delta G^{\ddagger} = 13.0$ kcal/mol, which is substantially larger than the previous prediction.[13] This reaction is symmetry allowed and it is surprising that the predicted barrier is still half of that for **1**. However, aside from a modestly lengthened σ bond, the early transition state structure is minimally changed from **4**, presumably because of the peculiar ring constraints. This provides little strain relief in the transition state and thus the barrier remains high. We did not attempt to locate the symmetry-forbidden transition state for disrotatory opening of **4** to **3**, which must be at an even higher energy.

By comparison to **1**, the 1.518-Å intraannular C−C bond distance in **4** is unusually short. Wiberg observed a similar result with *trans*-bicylo[2.2.0]hexane and attributed this to a twisted σ bond that attempts to increase overlap.[30] In response to the earlier challenge by Woodward and Hoffmann,[9] we can now calculate an expected lifetime for **4**. Based on our calculated $\Delta G^{\ddagger}$ of 12.7 kcal/mol for ring opening, we estimate a half-life of 0.2 ms at 25 °C.

Conclusions

Four complementary modes of reaction (Scheme 1) connect Dewar benzene (**1**) and its trans isomer (**4**) with benzene, the global minimum. Our calculations first predict the existence of *cis,cis,trans*-1,3,5-cyclohexatriene (**3**), a benzene valence isomer that has been the subject of speculation during the past 30 years.[2,5,16] Because of the very small barrier for π bond rotation, this species will be difficult to detect, and it seems unlikely that **3** lies on the route to other benzene isomers such as benzvalene. Further work is necessary to resolve this question. Structure **3** has been referred to as Möbius benzene; we support usage of this name because the π orbital basis in **3** does define a Möbius topology.

Electrocyclic ring opening of Dewar benzene (**1**) has long been assumed to be disrotatory.[7−13,24] Contrary to this assumption, our calculations indicate that conrotatory opening of **1** to **3** proceeds through a slightly *lower* energy transition state than disrotatory opening to **2**. Our predicted barriers of 24−28 kcal/mol agree well with the experimental value of 25.1 ± 2. Thus, despite formidable ring constraints and the formation of an extraordinarily strained initial product, orbital symmetry control triumphs in a case long maintained as a paradigm for a symmetry-forbidden reaction.[7,8] Many derivatives of Dewar benzene have been studied; we cannot yet predict whether the conrotatory path will also be lower for these substances.[31]

Our calculations support the existence of another new benzene isomer, *trans*-Dewar benzene (**4**). This interesting substance was first suggested by Woodward and Hoffmann in 1971 and later studied through MNDO calculations by Dewar and coworkers in 1977, but then seems to have been entirely forgotten. Our predicted barrier for conrotatory ring opening to benzene is sufficiently large that **4** might be observed by spectroscopic methods. However, at ca. 158 kcal/mol above benzene, *trans*-Dewar benzene is so high in energy that it may be impossible to prepare. No successful synthesis of the saturated derivative, *trans*-bicyclo[2.2.0]hexane, has yet been reported.

We have studied these structures at a level of theory that generally yields reliable results for pericyclic reactions and strained hydrocarbons. Thus, we believe our calculations suggest revision of some long-held views in benzene chemistry. Undoubtedly, many other surprises remain to be discovered on the C_6H_6 potential surface.

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Supporting Information Available: Cartesian coordinates for stationary points (4 pages). See any current masthead page for ordering and Internet access instructions.

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