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Structure, Strain Energy, and Magnetic Susceptibility of [4]Paracyclophane and the Activation Energy for Its Interconversion with 1,4-Tetramethylene Dewar Benzene

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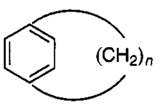
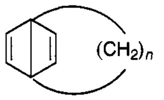
Abstract: *Ab initio* quantum mechanical methods were employed to study [4]paracyclophane and its Dewar benzene isomer at the self-consistent-field (SCF), two configurations SCF (TCSCF), configuration interaction with single and double excitations from two reference functions (TCSCF CISD) and second-order perturbation (MP2) methods. The quantities predicted include their equilibrium geometries, harmonic vibrational frequencies, the energy difference and activation energy for the interconversion between the two isomers, the evaluation and partition of the strain energy for [4]paracyclophane, and the magnetic susceptibility. Unlike previous results for the energy difference between [4]paracyclophane and its Dewar benzene isomer form (3.0 kcal mol^{-1}), this energy difference is predicted to be 9 kcal mol^{-1} at the DZ+d TCSCF CISD+Q level. The activation energy for the isomerization from Dewar benzene isomer is predicted to be 32 kcal mol^{-1} at the DZ+d TCSCF CISD+Q level. The activation energy for the back isomerization from the benzene form to the Dewar benzene form is 21 kcal mol^{-1} at the DZ+d TCSCF CISD+Q level, which explains the thermal stability of [4]paracyclophane against such a rearrangement. The strain energy for the [4]paracyclophane is estimated to be 85 kcal mol^{-1} at the DZP MP2 level via the appropriate homodesmotic reaction. Our subpartitioning of the strain energy in benzene indicates that the conjugation energy may be lost. Therefore it is difficult to classify [4]paracyclophane as aromatic on the basis of conjugation energy. However, our study shows that the degree of bond alternation in the C_6 ring in [4]paracyclophane is only 0.02 Å at both SCF and MP2 levels, and this may represent a lower limit. The extent of bond alternation increases to 0.087 Å at the DZ+d TCSCF level, which is certainly the upper limit value for bond alternation. The small degree of bond alternation supports recent theoretical proposals that the driving force for the D_{6h} benzene structure is σ bonding. An important finding in this study is that the boat-shaped benzene (with the same geometry as in [4]paracyclophane) has the same magnetic susceptibility as the hypothetical cyclohexatriene. Therefore a weak ring current is expected in [4]paracyclophane. However, whether [4]paracyclophane could be classified as aromatic on the basis of magnetic susceptibility depends on how one classifies the hypothetical cyclohexatriene.

1. Introduction

One of the intriguing aspects of aromaticity is the question of how much bending a benzene ring can tolerate without losing its aromatic character.[1] Distortions from the benzene structure may be achieved by connecting its para positions by a short oligomethylene bridge. Molecules of this type—[*n*]paracyclophanes (**I**)—have received considerable theoretical and experimental attention in recent years.[1−11] The thermal stability of [*n*]paracyclophanes decreases with decreasing chain length. Thus, [7]- and [6]paracyclophane are relatively stable.[2] However, [5]paracyclophane has not been isolated in a pure form at room temperature[3] and [4]paracyclophane has only been prepared as a transient species via matrix isolation.[4] Even though [5]paracyclophane was predicted[8] to be thermochemically more stable than its Dewar benzene isomer (**II**), it is more reactive and is produced via photochemical reactions starting with the Dewar benzene type compound **II**. In contrast, [4]paracyclophane[7] has been predicted to lie higher in energy than its Dewar benzene isomer.



I



II

Both [4]- and [5]paracyclophane are important in answering the question of how bent a benzene can be. The question of whether [5]- or even [4]paracyclophanes are aromatic has been the subject of controversy. On the basis of on the UV and ^1H

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Table 1. The Equilibrium Geometries of [4]Paracyclophane and 1,4-Tetramethylene Dewar Benzene (Bond Distances in Å and Bond Angles in Deg)

		DZ+d SCF	DZP SCF	TZ2P SCF	DZ+d BLYP	DZ+d B3LYP	DZ+d MP2	DZ+d TCSCF
[4]paracyclophane	r_1	2.661	2.660	2.647	2.723	2.696	2.707	2.722
(Figure 1a)	r_2	1.386	1.386	1.378	1.410	1.399	1.403	1.353
	r_3	1.399	1.399	1.392	1.428	1.415	1.419	1.440
	r_4	1.399	1.399	1.391	1.428	1.415	1.419	1.439
	r_5	1.519	1.519	1.516	1.534	1.523	1.516	1.524
	r_6	1.593	1.592	1.593	1.616	1.600	1.590	1.575
	r_7	1.582	1.582	1.581	1.592	1.581	1.577	1.568
	α	38.2	38.1	38.0	38.8	38.8	39.7	42.7
	β	29.8	29.9	29.7	30.0	30.0	29.4	28.2
1,4-tetramethylene Dewar benzene	r_1	1.564	1.565	1.565	1.607	1.589	1.589	1.564
(Figure 1b)	r_2	1.328	1.328	1.319	1.360	1.348	1.361	1.330
	r_3	1.529	1.529	1.527	1.547	1.536	1.529	1.528
	r_4	1.530	1.530	1.528	1.552	1.539	1.532	1.530
	r_5	1.532	1.531	1.528	1.548	1.536	1.530	1.529
	r_6	1.536	1.535	1.533	1.557	1.544	1.539	1.537
	r_7	1.534	1.532	1.530	1.553	1.541	1.536	1.535

NMR spectra, Jenneskens *et al.* concluded[3a] that "the benzene ring (of [5]paracyclophane) retains its aromatic character with a remarkable tenacity". The even more severely strained [4]-paracyclophene,[4] which a more bent benzene ring than the [5]-paracyclophane, also has a strong UV absorption around 260 nm and displays red-shifted absorption bands at 330−340 and 370−380 nm. The dispute[3,6] over the aromatic character of [5]-paracyclophane is robust, since there is no unique operational definition of aromaticity. Five qualitative views of the aromaticity (or lack thereof) of [5]paracyclophane have been suggested.[6] Three of these criteria indicated that [5]paracyclophane may be judged not to be aromatic: (1) the high chemical reactivity of [5]paracyclophane ([5]paracyclophane undergoes addition rather than substitution reactions at the para positions[3]); (2) the substantial nonplanarity of the benzene ring ($\beta = 24°$ defined as in Figure 1a):[6,8,9] and (3) the high strain energy (78 kcal mol^{-1}) for [5]paracyclophane.[6,8,9] However, two criteria indicate that [5]paracyclophane may be judged to be aromatic: (1) the close correspondence between the predicted vibrational frequencies of [5]paracyclophane and *p*-dideuteriobenzene[6] and (2) the very small (0.025 Å),[6,8,9] geometrical extent of bond alternation of the benzene ring.

Following the example of [5]paracyclophane, a quest into the aromaticity of [4]paracyclophane is desired. [4]Paracyclophane may be the smallest paracyclophane that can be made. There are several theoretical studies of [4]paracyclophane, most of them being with semiempirical methods. The high-level *ab initio* study by Grimme appeared in 1992. Grimme has shown that the degree of bond alternation in the C_6 ring is still small (Table 1) in [4]paracyclophane. Grimme[7] pointed out that the small degree of bond alternation in the distorted benzene ring and the benzene-like excited state shows that some benzenoid character is retained due to the topology of the carbon skeleton, even though he also suggested that [4]paracyclophane is best classified as a strained molecule with partial diradicaloid character. However, there are several questions unresolved by Grimme's study: (1) As pointed by Grimme, [4]paracyclophane is best classified as a strained molecule with partial diradicaloid character. Therefore, how does bond alternation in the C_6 ring change with the inclusion of electron correlation effects and the addition of a second reference configuration to the theoretical description? (2) Experimentally, the [4]paracyclophane molecule is stable against a thermal back reaction to the Dewar benzene form; so what is the activation energy for the interconversion between the benzene form and the Dewar benzene form?

Augmented with the previous studies[6] of [*n*]paracyclophanes performed in our group, we report a theoretical study of [4]-paracyclophane herein. Particular attention is focused on the above questions and the magnetic susceptibility of [4]paracyclophane. The most widely used method for determining aromaticity has been the observation of diamagnetic anisotropy in the ^{1}H NMR spectrum. It has been suggested that the large diamagnetic anisotropy in benzene is due to the ring current in benzene.[12a] Very recently, Fleischer, Kutzelnigg, Lazzeretti, and Mühlenkamp (FKLM)[12b] presented an IGLO study of benzene and some related molecules to examine the evidence for the ring current model. Evidence is accumulated that the increased magnetic susceptibility in benzene comes from the π electron system and is an indication of a nearly free circular current in the π system of benzene. Therefore, a theoretical study of the magnetic susceptibility for distorted benzene will open an additional window to the question of how bent a benzene can be.[12c]

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2. Theoretical Methods

Three basis sets are employed in this study. The first, designated DZ+d, is the standard Huzinaga–Dunning contracted Gaussian basis[13] C(9s5p/4s2p), H(9s/4s) augmented with a set of (five) d functions on the carbon atoms [$\alpha_d(C) = 0.75$]. The second, a double-ζ plus polarization (DZP) quality, is this standard Huzinaga–Dunning contracted Gaussian basis[13] augmented with a set of (five) d functions on the carbon atoms [$\alpha_d(C) = 0.75$] and a set of p functions on the hydrogen atoms [$\alpha_p(H) = 0.75$]. The third, designated triple-ζ plus double polarization (TZ2P), is the Huzinaga–Dunning C(10s6p/5s3p), H(5s/3p) contracted Gaussian basis[13] augmented with two sets of (five) d functions [$\alpha_d(C) = 1.50, 0.35$] on the carbon atoms and two sets of p functions [$\alpha_p(H) = 1.50, 0.35$] on the hydrogen atoms.

The structures of both [4]paracyclophane and its Dewar benzene isomer were fully optimized using the self-consistent-field (SCF), two-configuration SCF (TCSCF)[14,15] and second-order perturbation[16] (MP2) methods. The consideration of the TCSCF wave function is desired because the interconversion of the two isomers involves the breaking of a C–C bond. The potential energy surface connecting the two isomers may be discontinuous otherwise, since the thermal isomerization process is symmetry forbidden. The TCSCF wave functions may also be necessary to account for the diradicaloid nature[7] of [4]paracyclophane. The two configurations (both of C_2 symmetry) employed are the following: (1) the single determinant electronic configuration of ground state [4]paracyclophane and (2) the configuration arising from the double excitation of the first configuration from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This second configuration is identical with the single determinant electronic structure for ground state 1,4-tetramethylene Dewar benzene; therefore, it may be referred to as Dewar benzene like. The TCSCF wave functions involve simultaneous optimization of the coefficients of the two configurations as well as the molecular orbital (MO) expansion coefficients. A DFT calculation which is less sensitive to multireference effects is also performed to optimize the structures of both [4]paracyclophane and its Dewar benzene isomer.

Configuration interaction wave functions including all single and double excitations[17] (CISD) were determined at the SCF and TCSCF optimized geometries. With the CISD method the ten core molecular orbitals (carbon 1s-like) were kept doubly occupied in all configurations, and the ten highest virtual molecular orbitals were likewise deleted. Otherwise, all single and double excitations from the SCF or TCSCF reference configurations were included (TCSCF CISD), giving 2 772 225 and 5 536 857 configurations in C_2 symmetry at the DZ+d CISD and DZ+d TCSCF CISD levels, respectively. The contributions from unlinked cluster quadruple excitations to the CISD energies were estimated using the Davidson correction[18] and its two-reference analog, and the results incorporating this refinement are denoted CISD+Q and TCSCF CISD+Q, respectively.

The magnetic susceptibilities were evaluated using the IGLO method.[19] In order to compare with the literature, all calculations were done with "basis sets II", which is of TZP quality.[12b] The Huzinaga basis sets,[13] recommended by Kutzelnigg et al.,[19] were employed and were contracted as follows: C 9s5p1d contracted to [51111,2111,1] [$\alpha_d(C) = 1.0$] and H 4s1p contracted to [311,1] [$\alpha_p(H) = 0.7$].

Harmonic vibrational frequencies were determined using analytic second derivative methods at the SCF level. The enthalpy changes were evaluated as follows:

$$\Delta H^\circ = \Delta E_e + \Delta E_v^\circ + \Delta(\Delta E_v)^{298} + \Delta E_r^{298}$$

Where ΔE_e is the energy difference without zero-point energy (ZPVE) correction, ΔE_v° is the difference between the zero-point vibrational energies of reactant and product at 0 K, $\Delta(\Delta E_v)^{298}$ is the change in the vibrational energy difference in going from 0 to 298 K, and ΔE_r^{298} is rotational energy at 298 K. The computations were performed using the program PSI developed by this research group,[20] the program Turbomol,[21] and the program Gaussian 92.[22]

3. Results and Discussion

A. Structures and Vibrational Frequencies of [4]Paracyclophane and Its Dewar Benzene Isomer. The structures of [4]paracyclophane and its Dewar benzene isomer are reported in Figure 1 and Table 1. For both isomers the geometries at the DZ+d SCF and DZP SCF levels are similar, consistent with the results of Grimme.[7] The bond distances are somewhat shorter with the basis set extended to TZ2P in the present work; the C=C double bond distances decrease by 0.007–0.008 Å from DZP to TZ2P. The critical bending angles α and β change by only 0.1° and 0.2°, respectively, from DZP SCF to TZ2P SCF. Thus it is concluded that basis set extension has relatively minor effects on the geometries of the two isomers and that the DZ+d basis set is sufficient for qualitatively describing the geometries for the two isomers. The bond distances for the benzene skeleton of [4]paracyclophane are longer (up to 0.028 Å, r_4) at the DZ+d MP2 level than that at the DZ+d SCF level. At the MP2 level the r_1 and r_2 distances for the Dewar benzene isomer (Figure 1b) are also significantly longer (by up to 0.042 Å, r_2) than that at the SCF level.

Grimme[7] has pointed out that [4]paracyclophane is the borderline case for the applicability of single-reference determinant approaches. One way to begin to overcome this deficiency is to use TCSCF wave functions. Therefore, we optimized the geometries of both [4]paracyclophane and its Dewar benzene isomer at the DZ+d TCSCF level. The geometry of [4]paracyclophane at the DZ+d TCSCF level differs significantly from that at single-reference determinant levels (both SCF and MP2). The extent of bond alternation in the C_6 ring is less than 0.02 Å at both SCF and MP2 levels and using the popular density functional methods[22] BLYP and B3LYP (Table 1). However, the bond alternation increases to 0.087 Å at the DZ+d TCSCF level. Therefore, the geometry of [4]paracyclophane is diradical-like (with the radical sites localized at the para positions) at the TCSCF level.

Here an examination of the reliability of the TCSCF treatment is in order. The question is whether the TCSCF results correctly reflect the diradicaloid nature of [4]paracyclophane or instead that the TCSCF structure is simply an artifact. For this purpose we may compare the DZ+d SCF and DZ+d TCSCF geometries for both 1,4-tetramethylene Dewar benzene and benzene. As can be seen in Table 1, the geometries of 1,4-tetramethylene

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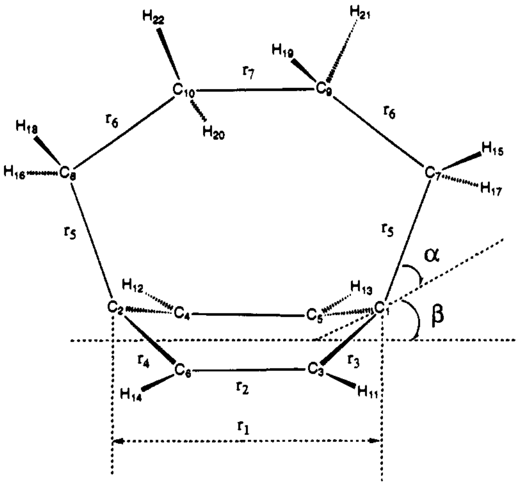
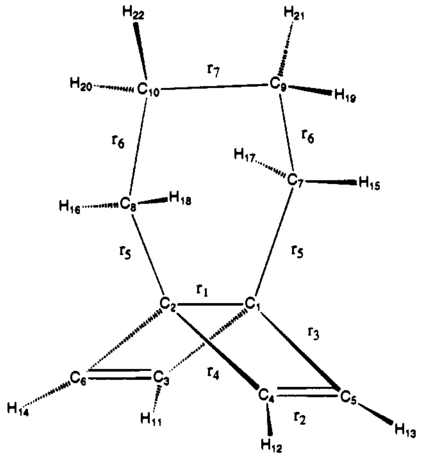
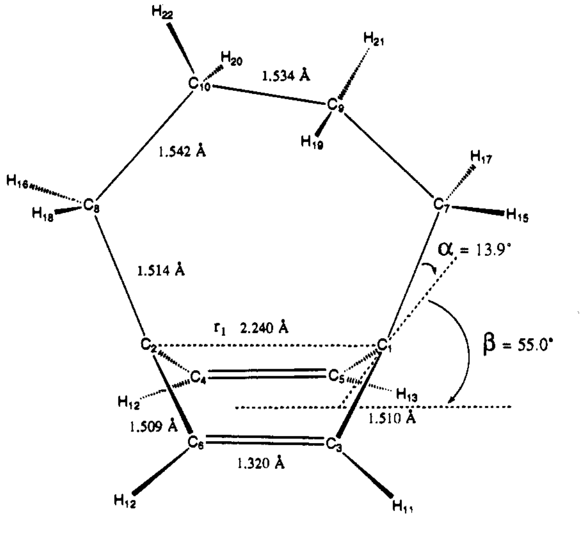


a. C_2 [4] Paracyclophane



b. C_2 1,4 Tetramethylene Dewar Benzene



c. C_2 Transition State

Figure 1. (a) Definition of the structural parameters of [4]paracyclophane. (b) Definition of the structural parameters of 1,4-tetramethylene Dewar benzene. (c) The geometry of the transition state for the interconversion of the two isomers at the DZ+d TCSCF level of theory.

Dewar benzene are almost identical at the DZ+d SCF and DZ+d TCSCF levels. Therefore, we conclude that the large degree of bond alternation in [4]paracyclophane at the DZ+d TCSCF level is consistent with a diradicaloid nature. Further evidence for this conclusion may come from the analysis of the coefficients for both configurations. As can be seen in Table 3, [4]paracyclophane has significant contributions from both configurations. However, the bond alternation in the C_6 ring at the DZ+d TCSCF level may only be thought as the upper limit for the bond alternation in the C_6 ring in [4]paracyclophane. The TCSCF CISD method will certainly narrow the bond alternation. Our most reliable structure for [4]paracyclophane is the DZ+d MP2 structure. However, the 5 536 857 configurations arising in the DZ+d TCSCF CISD level prevent the full optimization of the geometry and only single point energies at the DZ+d TCSCF optimized structures were obtained.

Besides the extent of bond alternation, the vibrational frequencies of [4]paracyclophane may be another criteria for judging the "aromatic" character of the cyclophane via comparison with those of benzene. The Berkeley group[6] studied the harmonic vibrational frequencies of [5]paracyclophane at the DZ SCF level. They found that the vibrational frequencies of [5]paracyclophane are surprisingly close to their counterparts for benzene and the theoretical harmonic frequencies lie 10% above the experimental anharmonic frequencies (Table 4); such errors are indeed typical at the DZ SCF level of theory. A similar situation has been observed in the present study of [4]-paracyclophane at the DZP SCF level. As indicated in Table 4 there are some similarities between the vibrational frequencies of benzene (or *p*-dimethylbenzene) and those of [4]paracyclophane at the DZP SCF level. However, at the DZ TCSCF level, the vibrational frequencies for the comparable C=C stretches in the C_6 ring differ substantially, with two C=C stretch modes (1656 and 1638 cm^{-1}) in [4]paracyclophane being 100 cm^{-1} lower than these for benzene (1764 and 1762 cm^{-1}). The vibrational frequencies of [4]paracyclophane are more sensitive to the consideration of TCSCF wave functions than in the case of benzene. For the benzene molecule, the theoretical vibrational frequencies at the DZP SCF, DZ SCF, and DZ TCSCF levels are close. However, for [4]paracyclophane, the vibrational frequencies for the two C=C stretch modes at the DZ TCSCF level are 80 cm^{-1} lower than these are the DZP SCF level, consistent with the larger degree of bond alternation at the TCSCF level than at the SCF level.

B. Relative Energies for [4]Paracyclophane and Its Dewar Benzene Isomer. The total energies and relative energies for [4]paracyclophane and its Dewar benzene isomer are reported in Table 2. The relative energies show little basis set dependence at the SCF level. However, only the DZ+d basis set is applicable at the TCSCF and MP2 levels. [4]Paracyclophane lies around 18 kcal mol^{-1} higher in energy than its Dewar benzene isomer at the SCF level. However, at the TCSCF and MP2 levels the energy difference decreases to around 3 kcal mol^{-1}. Grimme[7] obtained the MP2 energy difference at his DZP SCF optimized geometries and his results are similar to ours. Grimme pointed out that the correlation energy correction is larger for [4]paracyclophane, as indicated by the smaller isomerization energy at the MP2 level for the two isomers. However, the MP2 energy difference should be taken with caution. Firstly, the DZ+d CISD energy difference (Table 2) is still as large as 15 kcal mol^{-1}. Secondly, when the TCSCF treatment is under consideration, the correlation energy corrections are larger for the Dewar benzene form. This may be illustrated by the increasing energy difference from TCSCF to TCSCF CISD to TCSCF CISD+Q (Table 2). It was found[8,10] that for $n = 5$, 6, and 7 systems, the correlation energy corrections are also larger for the Dewar benzene form. Therefore, this trend holds for the $n = 4$ system and the TCSCF results are more reliable than those at the MP2 level. The

Table 2. The Total Energies (hartree) of [4]Paracyclophane and 1,4-Tetramethylene Dewar Benzene and the Thermochemistry of Their Interconversion (kcal mol^{-1})

	[4]paracyclophane	1,4-tetramethylene Dewar benzene	isomerization energy[d] ([4]paracyclophane to 1,4-tetramethylene Dewar benzene)			barrier height[e-g] ([4]paracyclophane to 1,4-tetramethylene Dewar benzene)		
theoretical level	total energy	total energy	ΔE_e	ΔE_0	$\Delta H°$	ΔE_e	ΔE_0	$\Delta H°$
DZ+d SCF	−385.558 01	−385.586 86	18.1	17.5	17.5			
DZP SCF	−385.579 87	−385.609 04	18.3	17.7	17.7			
TZ2P SCF	−385.631 24	−385.659 65	17.8	17.2	17.2			
DZ+d BLYP	−387.975 01	−387.971 13	−2.4	−3.0	−3.0			
DZ+d B3LYP	−388.189 08	−388.192 60	2.2	1.6	1.6			
DZ+d MP2	−386.842 97	−386.848 55	3.5	2.9	2.9			
DZP MP2[a]	−387.088 64	−387.093 38	3.2	2.6	2.6			
DZ+d CISD[b]	−386.552 86	−386.578 20	15.9	15.3	15.3			
DZ+d CISD+Q[b]	−386.765 85	−386.788 55	14.2	13.6	13.6			
DZ+d TCSCF	−385.588 85	−385.593 84	3.1	2.5	2.5	(21.1) 17.9	(19.0) 16.3	(19.2) 16.6
DZ+d TCSCF CISD[c]	−386.568 72	−386.582 64	8.7	8.1	8.1	(30.8) 22.0	(28.7) 20.4	(28.9) 20.7
DZ+d TCSCF CISD+Q[c]	−386.776 31	−386.792 06	9.9	9.3	9.3	(33.1) 23.2	(31.6) 21.6	(31.8) 21.9

[a] Single-point energies at the DZP SCF optimized geometries. [b] Single-point energy at the DZ+d SCF optimized geometries. [c] Single-point energy at the DZ+d TCSCF optimized geometries. [d] Vibrational frequencies are obtained at the DZP SCF level. [e] Vibrational frequencies are obtained at the DZ TCSCF level. [f] Total energies of the transition state: −385.56050 (DZ+d TCSCF), −386.53405 (DZ+d TCSCF CISD), and −386.73982 (DZ+d TCSCF CISD+Q). [g] The value in parentheses is the barrier height from 1,4-tetramethylene Dewar benzene to [4]paracyclophane.

Table 3. The Coefficients[a] for the Two Configurations in the TCSCF Wave Functions

[4]paracyclophane		transition state		1,4-tetramethylene Dewar benzene	
C_1	C_2	C_1	C_2	C_1	C_2
0.917	0.400	0.472	0.882	0.099	0.995

[a] The first configuration (C_1) is benzene-like and the second configuration (C_2) is Dewar benzene-like.

different correlation effects at the MP2 level and the TCSCF CISD level indicate that the single determinant methods are not sufficient for [4]paracyclophane.

Our most reliable prediction for ΔE_e ([4]paracyclophane − 1,4-tetramethylene Dewar benzene) is the DZ+d TC-CISD + Q prediction of 9.9 kcal mol^{-1}. Correction for ZPVE decreases this to $\Delta E_0 = 9.3$ kcal mol^{-1}, and further correction to room temperature yields the same result, $\Delta H° = 9.3$ kcal mol^{-1}.

Second-order perturbation theory often overcorrects for the effects of electron correlation. Thus one might expect the true energy difference between [4]paracyclophane and its Dewar benzene isomer to lie between 18 (SCF) and 3 kcal mol^{-1} (MP2). The TC-CISD + Q result of 9 kcal mol^{-1} nicely matches this anticipation.

However, it is possible that the MP2 result may be closer to the truth than is TC-CISD + Q. We have also optimized the structures of both [4]paracyclophane and its Dewar benzene form using the popular density functional methods[22] BLYP and B3LYP. The same DZ+d basis set described above was used in both density functional approaches. The B3LYP energy difference ΔE_0 is 2.2 kcal mol^{-1}, very close to the MP2 value (3.5 kcal mol^{-1}), while the BLYP method actually predicts [4]-paracyclophane to lie *lower* by 2.4 kcal mol^{-1}. It would certainly be desirable to apply higher level theoretical methods to this problem.

C. Transition State and Activation Energy for the Interconversion between [4]Paracyclophane and Its Dewar Benzene Isomer. The location of the transition state for the isomerization requires special consideration due to the fact that this isomerization is symmetry forbidden. Bockish[10] *et al.*, in order to circumvent the problem, used a "chain method" to locate the transition states for the isomerizations of [7]- and [6]paracyclophane to their Dewar benzene isomers. However, in our study at the TCSCF level there is no such problem, because the TCSCF wave function includes the electronic configurations for both the benzene and Dewar benzene forms. The TCSCF wave function coefficients for the two reference configurations vary smoothly. Therefore, the potential energy surface connecting the two isomers is continuous at the TCSCF level.

The transition state located at the DZ+d TCSCF level is indicated in Figure 1c. At the transition state the reaction coordinate distance $r_1(C_1-C_2) = 2.244$ Å. With the semiempirical MNDO method, Bockisch *et al.* have obtained[10] $r_1 = 1.97$ Å for the transition state between unsubstituted benzene and Dewar benzene, $r_1 = 2.01$ Å for [7]paracyclophane, and $r_1 = 2.10$ Å for [6]paracyclophane. Therefore, the reaction coordinate distance appears to increase with decreasing chain length.

The activation energy (Table 2) for the isomerization from [4]paracyclophane to the Dewar benzene form is $\Delta E_0 = 16.3$ kcal mol^{-1} at the DZ+d TCSCF level and $\Delta E_0 = 20.4$ kcal mol^{-1} at the DZ+d TCSCF CISD level. Usually, correlation effects lower the barrier heights for chemical reactions. However, correlation effects increase the barrier height by 4.1 kcal mol^{-1} for the isomerization between [4]paracyclophane and its Dewar benzene isomer. Our observation is consistent with the results of Bockisch[10] *et al.*, whose semiempirical results show that correlation effects increase the barrier height by 12.2 and 12.4 kcal mol^{-1} for $n = 7$ and 6 system, respectively, with the MNDO method.

Our result for the activation energy for the isomerization is reasonable. There is no existing experimental value for the activation energy for the $n = 4$ system. However, experimentally, the comparable activation energy for the Dewar benzene isomerization of the $n = 6$ system[23] is 20.5 kcal mol^{-1}. Considering that the decrease of the chain length for 6 to 4 will increase the strain energy at the transition state, the increase of the activation energy for the $n = 4$ system to 30.7 kcal mol^{-1} is within one's expectations. The increasing of the activation energy with decreasing chain length is also consistent with experimental observations. The Dewar benzene isomers for $n = 6$, 5, and 4 are able to be thermolyzed (flow pyrolysis).[4a]

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[23] Dreeskamp, H.; Kapahnke, P.; Tochtermann, W. *Radiat. Phys. Chem.* **1988**, *32*, 537.

Table 4. Selected Harmonic Vibrational Frequencies (cm^{-1})[a] for [4]Paracyclophane Compared with the Analogous Features of Benzene

	[4]paracyclophane		[5]paracyclophane	*p*-dimethylbenzene	benzene			
mode[a]	DZP SCF	DZ TCSCF	DZ SCF[b]	DZP SCF	DZP SCF	DZ SCF	DZ TCSCF	experiment[b]
C−H	3360, 3357	3394, 3389	3391, 3386	3360, 3351	3385, 3374	3422, 3406	3421, 3405	3074, 3057
C−H	3338, 3337	3365, 3365	3365, 3362	3339, 3331	3356, 3346	3384, 3373	3383, 3371	3057
C═C	1731	1656	1765	1817	1784	1782	1764	1610
C═C	1712	1638	1739	1764	1784	1782	1762	1610
C═C	1622	1601	1650	1680	1629	1636	1636	1484

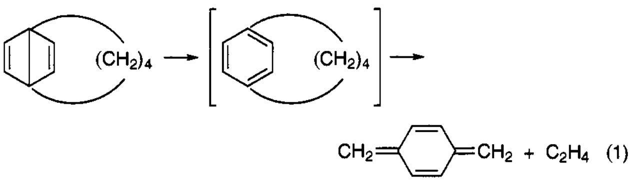
[a] The selected vibrational frequencies are those assigned to the benzene ring moiety. For the procedure used in making these assignments, see ref 6. [b] Reference 6a.

Table 5. Partitioning of the Strain Energy (kcal mol^{-1}) in [4]Paracyclophane[a]

	total strain energy[b,c]				subpartitioning of the strain energy due to benzene deformation			
theoretical level	ΔE_e	ΔE_0	ΔH°	chain	benzene deformation	α[d] deformation	β[e] deformation	loss of resonance[f]
DZP SCF	109.5	106.9	107.1	12.4	95.0	30.1		
					(97.0)	(30.5)	(29.5)	(37.0)
DZP MP2	85.0	82.4	82.6	12.2	78.2	24.7		
					(79.5)	(25.0)	(24.5)	(30.0)
DZ+d TCSCF					85.6	26.2	26.7	32.7
DZ+d TCSCF CISD					83.1	28.5	28.8	25.8

[a] The reference molecules are benzene and *p*-dimethylbenzene (in parentheses). [b] The total strain energy is evaluated by the homodesmotic reaction 1: $(CH_2)_4C_6H_4 + 5C_2H_6 \rightarrow H_3C{-}C_6H_4{-}CH_3 + 4C_3H_8$. [c] The MP2 energies are obtained at the DZP SCF optimized geometries, and the ZPVE are evaluated at the DZP SCF level. [d] β relaxing. [e] α relaxing. [f] Defined as strain energy (benzene deformation − α deformation − β deformation).

For example, for the $n = 4$ system there is the reaction



Experimentally,[4a] the temperature necessary for the thermolysis increases with decreasing chain length from $n = 6$ (60 °C) via $n = 5$ (285 °C) to $n = 4$ (300 °C), indicating the increasing activation energies.

D. Evaluation and Partitioning of the Strain Energy in [4]Paracyclophane. 1. Total Strain Energy and Its Partitioning. The strain energy for [4]paracyclophane may be evaluated using the homedesmotic reaction

$$(CH_2)_4C_6H_4 + 5C_2H_6 \rightarrow H_3C{-}C_6H_4{-}CH_3 + 4C_3H_8 \quad (2)$$

The strain energy obtained from reaction 2 is $\Delta E_e = 109.5$ kcal mol^{-1} at the DZP SCF level and 85 kcal mol^{-1} at DZP MP2 level (Table 5). If we use the experimental heats of formation[24] for C_2H_6 (−20 kcal mol^{-1}), C_3H_8 (−25 kcal mol^{-1}), and *p*-dimethylbenzene (4 kcal mol^{-1}), the heat of formation of [4]-paracyclophane is predicted to be 87.4 kcal mol^{-1}. A comparable value of 92.7 kcal mol^{-1} was obtained by the semiempirical AM1 method.[11]

The total strain energy for [4]paracyclophane may be partitioned into two parts, one being the strain energy due to the distortion of benzene and the other being the strain energy due to the distorted methylene chain. The common way[6−10] to partition is as follows: freezing the ring in the conformation present in [*n*]paracyclophane and placing the additional two hydrogen atoms at a typical C−H distance in the same direction as the first carbon atom in the chain; the energy difference of the distorted benzene and normal planar benzene is the strain energy resulting from the ring moiety. Similarly, the strain energy due to chain strain may be obtained as well. The partitioning results are reported in Table 5; similar results were obtained by Grimme.[7] What is new in the present analysis is that, in order to partition more accurately, i.e., to consider the substitution effects of the methylene chain, we also studied the energy difference for the distorted and undisturbed *p*-dimethylbenzene molecule in the manner discussed above. Interestingly, this procedure yields similar results.

The sum of the strain energy due to the benzene and that of the chain is 90 kcal mol^{-1}, which is a little higher than the total strain energy (85 kcal mol^{-1}) obtained via the homodesmotic reaction 2 (see Table 5).

2. Subpartitioning of the Strain Energy Due to the Deformation of Benzene. The strain energy due to the benzene ring may be subpartitioned further to gain insight into the strain mechanism. The question is that within the 79 kcal mol^{-1} strain energy, how much is due to the nonplanerity of the C_6 skeleton, how much is due to the bending of the *p*-methylbenzene bonds (or para H−C bonds for benzene if using benzene as the strain free reference molecule), and how much is due to the loss of resonance energy. This subpartitioning has been accomplished as follows. The first step is "α relaxation"—freezing all the geometrical parameters except the methyl groups, r_5 distances, and α angle (Figure 1a), and optimizing the geometry; the strain energy obtained this way belongs to the deformation of the benzene carbon skeleton and is referred to as the β deformation (Figure 2, Table 5). The second step "β relaxation"—freezing the r_5 distance and the angle α (Figure 1a) and optimizing the benzene carbon skeleton; the strain energy obtained in this manner belongs to the distortion of the *p*-methylbenzene bonds (or para H−C bonds if using benzene as the strain free reference molecule) and is referred to as the α deformation (Figure 2, Table 5).

With the benzene C_6 skeleton constrained to the geometry of [4]paracyclophane, the "α relaxation" leads to geometries as in Figures 2a and 2c, for *p*-dimethylbenzene and benzene, respectively. The strain energy is around 25 kcal mol^{-1}. The above results corroborate with the study by Jenneskens, von

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(24) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

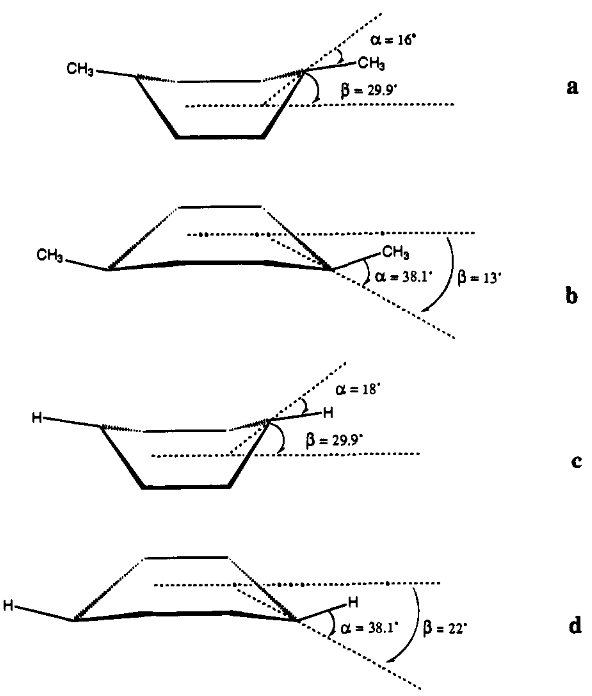

Figure 2. The structures resulting from the partial optimizations of *p*-dimethylbenzene and benzene starting from the corresponding conformation of [4]paracyclophane (Figure 1a) and following by partial relaxation: (a) *p*-dimethylbenzene, α angle optimized with the β angle frozen; (b) *p*-dimethylbenzene, β angle optimized with the α angle frozen; (c) benzene, α angle optimized with the β angle frozen; and (d) benzene, β angle optimized with the α angle frozen.

Eenige, and Louwen (JEL);[25] those authors studied the partially optimized benzene structures for various angles (β) of the out-of-plane bending of the C$_6$ skeleton using the semiempirical MNDO method and obtained similar structures and strain energies to that seen in Figure 2c. However, they did not study the small [*n*]paracyclophanes.

The results of the "β relaxation" are relatively complex. The benzene C$_6$ ring does not relax back to the ideal planar conformation. Instead, the β angle is inverted, leading to the conformations sketched in Figures 2b and 2d. This fact indicates that the α deformation and β deformation are strongly coupled. The strain energy obtained for the β deformation (α relaxation) is 25 kcal mol^{-1}. Note that the partitioning of the strain energy of the benzene (or dimethylbenzene) is 79 kcal mol^{-1}, whereas the sum of the strain energy of the α deformation and the β deformation is only 50 kcal mol^{-1}, i.e., 29 kcal mol^{-1} less. The contributions of the 29 kcal mol^{-1} additional strain energy may come from the coupling of the α deformation and the β deformation, and more importantly, the loss of resonance energy of benzene, as long as we assume that the partially optimized structures are still aromatic. The validity of this assumption may be illustrated by the examination of the π orbitals and magnetic susceptibilities of these partially optimized structures (next section). Further support of the assumption may come from recent theoretical work.[25,26] Specifically, Haddon has presented a method of analysis designated the p-orbital axis vector (POVA) which provides a clear picture of p-type bonding in distorted conjugated molecules in response to imposed nonplanarity.[26] The POVA analysis of unsubstituted boat-shaped benzene (with the conformations similar to those in Figure 5) was made by Jenneskens, von Eenige, and Louwen (JEL).[25] JEL found increasing rehybridization of the carbon atoms with progressing benzene distortion and that the rehybridization strongly facilitates electron conjugation and consequently electron delocalization in the partially relaxed benzene.

Table 6. Molecular Magnetic Susceptibility of the C$_6$H$_6$ System (ppm cgs, with Sign Reversed)

	this work				FKLM[a]			
	χ_{ip}	χ_{zz}	χ_{av}	$\Delta\chi$	χ_{ip}	χ_{zz}	χ_{av}	$\Delta\chi$
benzene	46.8	109.8	67.8	63.0	47.1	110.2	68.0	63.4
hypothetical cyclohexatriene					46.2	101.0	64.5	54.9
boat-shaped benzene (1)[b]	45.0	100.5	63.5	55.5				
boat-shaped benzene (2)[c]	44.9	101.6	63.8	56.7				
partially relaxed benzene (α)[d]	44.3	110	66.2	65.6				
partially relaxed benzene (β)[d]	44.8	103.7	64.5	58.9				

[a] Reference 12b. [b] The geometry is the same as in the DZ+d SCF optimized [4]paracyclophane. [c] The geometry is the same as in the DZ+d TCSCF optimized [4]paracyclophane. [d] Figure 2.

E. Molecular Orbitals of [4]Paracyclophane and the Diamagnetic Susceptibility of the Benzene Moiety. 1. Magnetic Susceptibilities of Benzene and Deformed Boat-Shaped Benzene. In order to compare with the magnetic susceptibility of unstrained benzene, we evaluated the magnetic susceptibilities of the boat-shaped benzene, whose geometry is the same as that of [4]paracyclophane; therefore, the conclusion drawn from the results of the boat-shaped benzene may be readily applicable for the parent molecule [4]paracyclophane. In order to study the mechanism of the change of magnetic susceptibilities in benzene, the magnetic susceptibilities for the partially relaxed structures (Figure 2) are also evaluated. The results are reported in Table 6, as well as other results (reference 12b). In Table 6, χ_{ip} is the average of the components χ_{xx} and χ_{yy}. Here χ_{zz} is the out-of-plane component. χ_{av} is the isotropic part, and the anisotropy $\Delta\chi$ is defined as $\Delta\chi = \chi_{zz} - \chi_{ip}$.

As may be seen in Table 6, we reproduce the literature value[12b] for the diamagnetic susceptibility for benzene; therefore, a direct citation of FKLM's results[12b] for other related species is warranted. In the following discussion, we concentrate on three questions: (1) the aromaticity of [4]paracyclophane in terms of magnetic susceptibility, (2) the possibility of ring currents in [4]paracyclophane, and (3) the factors affecting the magnetic susceptibility of benzene as a function of the out-of-plane deformation of benzene.

To answer the first question, a description of FKLM's results[12b] of a hypothetical planar cyclohexatriene will be helpful. FKLM studied a hypothetical cyclohexatriene with the following geometrical parameters: r(C=C) = 1.336 Å, r(C−C) = 1.501 Å, r(C−H) = 1.083 Å, and all angles equal to 120°. The interesting thing is that from the increment system adopted by FKLM, one predicts for benzene and its isomers [for instance, fulvene, dimethylenecyclobutene, and trismethylenecyclopropane][12b]

$$\chi_{ip} = -45.1 \text{ ppm cgs}; \qquad \chi_{zz} = -67.7 \text{ ppm cgs}$$

Therefore, in the hypothetical planar cyclohexatriene $|\chi_{zz}|$ is still 33 ppm cgs larger than for a molecule with isolated double bonds. Note that the bond alternation in the hypothetical cyclohexatriene is 0.165 Å, which is twice as large as our upper limit for [4]paracyclophane at the TCSCF level (0.087 Å). However, a simple glance at Table 6 will show that the boat-shaped benzene (with the same geometry as appeared in [4]-

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[25] Jenneskens, L. W.; von Eenige, E. N.; Louwen, J. N. *New J. Chem.* **1992**, *16*, 775.

[26] (a) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676.

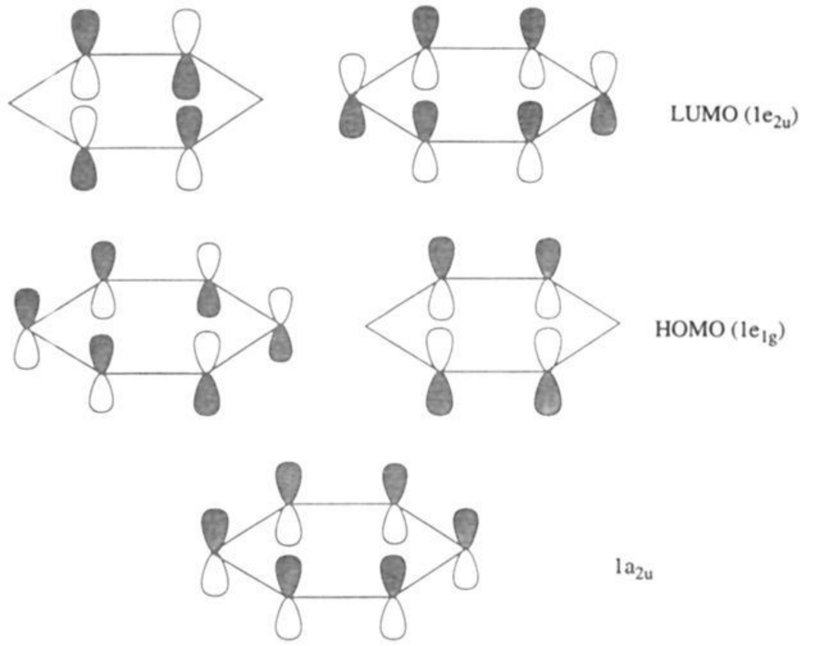

Figure 3. Schematic representation of the π molecular orbitals of benzene.

paracyclophane) has almost the same magnetic susceptibility as the hypothetical cyclohexatriene. Clearly, even though the extent of bond alternation is smaller in the boat-shaped benzene, the nonplanarity further reduces the magnetic susceptibility. On the basis of the magnetic susceptibility, therefore, whether [4]-paracyclophane should be classified as aromatic depends on that how one classifies the hypothetical planar cyclohexatriene.

As for the question of the possibility of ring currents in [4]-paracyclophane, we also seek the comparison with the hypothetical planar cyclohexatriene.[2b] FKLM's results indicated that the ring current is partially destroyed by distorting benzene to the hypothetical cyclohexatriene.[12b] Because the magnetic susceptibility of the boat-shaped benzene is the same as for the hypothetical planar cyclohexatriene, we conclude that the weak ring current may still be possible in [4]paracyclophane, which is consistent with the experimental claim that ring currents exist in [5]paracyclophane. However, the direct connection of the ring current in [4]paracyclophane and [5]paracyclophane with aromaticity will be questionable, because, as we stated earlier, it depends on that how one classifies the hypothetical planar cyclohexatriene.

A further examination of the diamagnetic susceptibility of the partially relaxed benzene reveals an important factor which primarily affects the magnetic susceptibility. Surprisingly, the χ_{zz} value of α-relaxed benzene (Figure 2c) has the same value as planar benzene (110 ppm cgs), while the magnetic susceptibility of the β-relaxed structure (Figure 2d) is significantly lower than those for α-relaxed benzene and unstrained benzene. Therefore, it is the nonplanarity of the C−H bond rather than the C_6 ring itself that diminishes the diamagnetic susceptibility.

2. Comparison of the Molecular Orbitals of Benzene and [4]Paracyclophane. The traditional mechanism for aromaticity involves the purported ability of π electrons ($4n + 2$) to be effectively conjugated and delocalized. For such a mechanism the planarity of the π system may be essential. However, the nonvanishing aromaticity in small [*n*]paracyclophanes is intriguing. Even for the smallest [*n*]paracyclophane—[4]paracyclophane—there are two features deserving discussion: (1) the small degree of bond alternation in the C_6 ring; and (2) the fact that the magnetic susceptibility of boat-shaped benzene (with the same geometry as [4]paracyclophane) is the same as that of the hypothetical planar cyclohexatriene, indicating a possible weak ring current in [4]paracyclophane.

The small bond alternation in the C_6 ring in [4]paracyclophane may be understood in terms of σ stabilization.[27] Recently, several theoretical studies[27] have challenged the traditional assumption that the driving force for the symmetrical structure of benzene relies on the delocalization of the $4n + 2$ π electrons. These quantum mechanical treatments suggest that the D_{6h} geometry of benzene is enforced by the σ electrons.[27] The structures of the small [*n*]paracyclophanes support this new explanation. Because the nonplanarity of benzene influences the π electrons mostly while the σ bonds are less sensitive, the extent of bond alternation in the small [*n*]paracyclophanes is small.

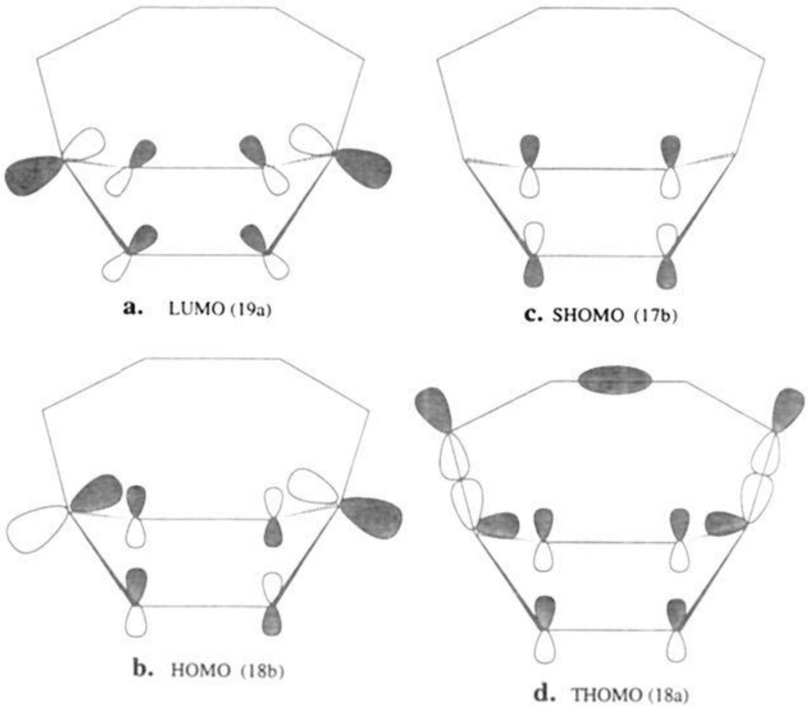

Figure 4. Schematic representations of selected molecular orbitals (MOs) of [4]paracyclophane. The MOs are simplified from the contour maps of the corresponding MOs: (a) the lowest unoccupied molecular orbital (LUMO), which is comparable to that of benzene (Figure 3); (b) the highest occupied molecular orbital (HOMO), which is comparable to that of benzene (Figure 3); (c) the second highest occupied MO (SHOMO), which is comparable to the $1e_{1g}$ MO of benzene (Figure 3); and (d) the third highest occupied MO (THOMO), which is comparable to the $1a_u$ MO of benzene (Figure 3).

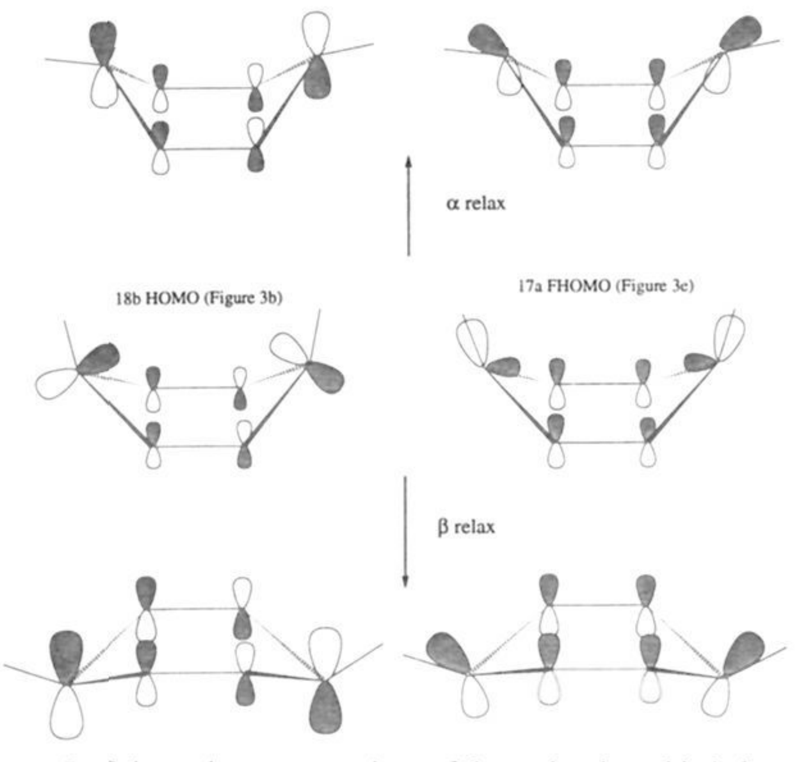

Figure 5. Schematic representations of the molecular orbital changes upon the angle α relaxing (upper) and the angle β relaxing (down), respectively. The two benzene-like π orbitals [HOMO and the fourth highest occupied MO (FHOMO)] of [4]paracyclophane that are unable to overlap effectively due to the distorsion of benzene ring (middle) recover their effective overlap after relaxing either the α angle or the β angle, even though the benzene ring is still nonplanar. The MO diagrams are simplified from their corresponding contour maps.

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(27) Gobbi, A.; Yamaguchi, Y.; Frenking, G.; Schaefer, H. F. *Angew. Chem., Int. Ed. Engl.* Submitted, and the references cited therein.

The ring current in the benzene system is apparently a π electron property. The question here is how to understand the possible weak ring current in boat-shaped benzene. For this purpose, we may compare the π molecular orbitals (MO) of benzene and the corresponding π MOs of [4]paracyclophane.

The π orbitals of benzene are indicated in Figure 3. The three highest occupied MOs as well as the lowest unoccupied MO (LUMO) of [4]paracyclophane are sketched in Figure 4. The schematic representation of the MO changes upon the relaxation of angles α and β is given in Figure 5. All these schematic representations of the MOs were deduced from their corresponding contour maps.

The HOMO and LUMO (Figure 4) for [4]paracyclophane are radical-like, since both MOs are essentially centered at the para position. This may explain the observed reactivity of [4]paracyclophane with respected to nucleophilic attack at these carbon atoms, a conclusion of which is also reached by Grimme.[7] Note that at the TCSCF level both HOMO and LUMO are partially occupied (occupancies: HOMO 1.68, LUMO 0.32). The comparison of the second highest occupied MO of [4]paracyclophane with the b component of the $1e_{1g}$ orbital of benzene indicates that this MO is essentially unperturbed by the deformation of benzene.

If the ring current exists in benzene, it is the $1a_{2u}$ orbital of benzene (Figure 3) that should contribute primarily, due to its totally delocalized nature. The $1a_{2u}$ orbital (Figure 3) is distorted in [4]paracyclophane, where the corresponding MO is the third highest occupied (THOMO, Figure 4d). Note the strange "p" type atomic orbitals at the para positions (Figures 4d and 5). In order to adjust to the bent α angle, the two lobes of this atomic p orbital are distorted to be perpendicular. However, this deformation does not break the π electron delocalization completely—the upper phase (the dark lobe) is still effectively delocalized. This may be the reason that the magnetic susceptibility of boat-shaped benzene still has the same value as for the planar hypothetical cyclohexatriene. The shape of this MO also indicates that the bending of the C−H bond will decrease the degree of π electron delocalization in the benzene ring. As may be seen from Figure 5, upon partial relaxation of the boat-shaped benzene, the effective overlap of π MOs returns, consistent with the quantitative analysis of the magnetic susceptibility in the previous section.

4. Conclusions

Unlike previous evaluations of the energy difference between [4]paracyclophane and its Dewar benzene isomer (3 kcal mol^{-1}),[7] this energy difference is predicted to be 9 kcal mol^{-1} at the DZ+d TCSCF CISD+Q level. A reasonable estimate of the uncertainty of the present prediction is ±4 kcal mol^{-1}. The activation energy for the isomerization from [4]paracyclophane is predicted to be 22 kcal mol^{-1} at the DZ+d TCSCF CISD+Q level by the present study, which explains the thermal stability of [4]paracyclophane against such back isomerization.

How much bending of a benzene ring can be tolerated without losing its aromatic character? The answer connot be definitive due to the lack of a general definition of aromaticity. The strain energy for [4]paracyclophane is estimated to be 85 kcal mol^{-1} at the DZP MP2 level via appropriate homedesmotic reaction. Our subpartitioning of the strain energy in benzene indicates that the conjugation energy may be lost in [4]paracyclophane. Therefore it is difficult to classify [4]paracyclophane as aromatic on the basis of conjugation energy. However, our study shows that the degree of bond alternation in the C_6 ring in [4]paracyclophane is around 0.02 Å at both the SCF and MP2 levels, which may be the lower limit. The bond alternation increases to 0.087 Å at the DZ+d TCSCF level, which certainly represent an upper limit value for the bond alternation. Considering that the bond alternation for the ideal single bond and double bond is around 0.16 Å, for example in a hypothetical planar cyclohexatriene,[12b] the bond alternation in [4]paracyclophane is still small. The small degree of bond alternation supports recent theoretical conclusions that the driving force for the D_{6h} structure of benzene is σ bonding.

An important finding in this study is that the boat-shaped benzene (with the same geometry as in [4]paracyclophane) has the same magnetic susceptibility as the hypothetical planar cyclohexatriene.[12b] Therefore a weak ring current is expected in [4]paracyclophane, while the classification of [4]paracyclophane as aromatic on the basis of magnetic susceptibility depends on how one classifies the hypothetical cyclohexatriene.

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