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Ab Initio Study of the Isomerization of Substituted Benzenes and [6]Paracyclophanes to the Dewar Benzene Isomers

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Abstract: The energy differences (ΔE) between the benzene and the corresponding Dewar benzene forms of seven substituted benzenes and three [6]paracyclophanes were calculated by ab initio methods with basis sets ranging from split valence type to triple-ζ plus polarization type. Correlation effects were taken into account using second-order Møller–Plesset perturbation theory (MP2). The results show that among all the investigated molecules the isomerization energy is largest for benzene itself; that is, benzene is 79 kcal/mol more stable than its Dewar form. Both, electron-accepting substituents and electron-donating substituents lower ΔE. Steric repulsion between substituents in the ortho position additionally destabilizes the benzene form relative to the Dewar form. [6]Paracyclophanes are influenced by substitution effects in the same way as the unbridged compounds. This finding can be interpreted as a further criterion for the aromaticity of the strongly deformed benzene ring in [6]paracyclophanes. Due to the deformation of the benzene ring, the ΔE values for the investigated [6]paracyclophanes are found to be considerably lower than those of the corresponding benzenes (about 25 kcal/mol). Our results are found to agree with the experimental isomerization enthalpies of hexamethylbenzene and perfluorohexamethylbenzene to within 5 kcal/mol, while a large discrepancy between theory and experiment is obtained for 8,9-dicarbethoxy[6]paracyclophane.

1. Introduction

Benzene is probably the molecule that has most attracted the attention of chemists, and there have always been intense discussions about its structure and the reasons for the exceptional thermodynamic stability of the planar $(CH)_6$ benzene ring. Any other $(CH)_6$ isomer is considerably higher in energy.[1] The most important of these valence isomers are Dewar benzene, prismane, and benzvalene, which can be obtained by irradiation of benzene. In the present paper we will concentrate on the Dewar isomer.

The isomerization reaction Dewar benzene → benzene is thermally forbidden according to the Woodward–Hoffmann symmetry rules.[2] It has been the subject of numerous theoretical investigations.[3-10]. Experimentally, kinetic parameters for this reaction involving various substituted compounds have been determined. However, very little thermodynamical data exist. For hexamethylbenzene, the measured values for the reaction enthalpy benzene → Dewar benzene (ΔH_R) range from 56 to 60 kcal/mol.[11-13] The latter value was considered by some authors to be equivalent to the corresonding value for benzene itself.[3,14] For perfluorohexamethylbenzene an extremely low value of 28 ± 1 kcal/mol was found.[15] This is an indication that the effects of substituents on the isomerization enthalpy can be quite strong.[12,16] Thus, the first aim of the present work is to use ab initio calculations to investigate the energy difference between Dewar benzene and benzene for a number of substituents. In particular it will be checked whether the assumption that the isomerization energy of hexamethylbenzene is the same as that of benzene is correct.

The family of [*n*]paracyclophanes[17,18] is related to the benzenes. In these compounds carbon 1 and carbon 4 of the benzene ring are connected by a chain of *n* (CH_2) groups. A long chain ($n \geq 8$) leaves the benzene ring planar, while shortening of the chain forces the benzene ring into a nonplanar boat-like geometry. This type of distortion can be looked upon as a deformation toward a Dewar benzene type structure. Shortening of the chain generally results in a reduction of the thermodynamical stability. There have been efforts to synthesize [*n*]paracyclophanes with *n* as small as possible. In 1972 [7]- and [6]paracylclophanes were successfully synthesized.[19] The formation of [5]- and [4]paracyclophanes has been reported recently.[20-22] The question of the aromaticity of the highly strained compounds has been discussed by several authors (see for example refs 23–26).

It has been found that the photochemical isomerization of [6]-paracyclophanes to the corresponding Dewar forms is reversible.[27,28] For the reaction 8,9–dicarbethoxy[6]paracyclophane → 8,9–dicarbethoxy[6]Dewar benzene a very low reaction en-

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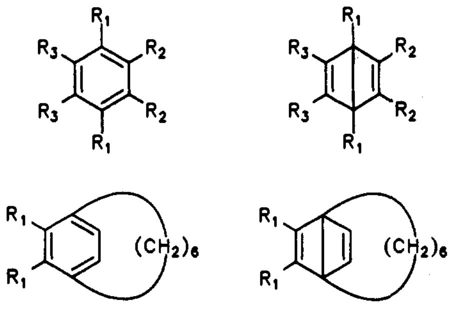

Figure 1. General structures of the benzene and Dewar forms of the benzene (upper) and [6]paracyclophane compounds (lower) treated in this work.

Table 1. Basis Set Description[a]

basis set	description	
SV	C, O, F	(7s,4p) → [3s,2p]
	H	(4s) → [2s]
DZP	C, O, F	(8s,4p) → [4s,2p] + d (0.8)
	H	(4s) → [2s] + p (0.8)
TZP	C, O, F	(10s,6p) → [6s,3p] + d (0.8)
	H	(5s) → [3s] + p (0.8)

[a] In the standard notation the number of primitive gaussians is given in parentheses, the corresponding number of contracted functions in brackets. SV stands for split valence, DZP and TZP for double-ζ plus polarization and triple-ζ plus polarization, respectively.

thalpy (5.6 kcal/mol) has been measured. For unsubstituted [*n*]paracyclophanes several ab initio calculations exist.[4,29–32] For these compounds considerably higher isomerization enthalpies[4] were found than in the experiments for the substituted compounds[28]. This difference (about 30–40 kcal/mol) is possibly due to substituent effects. The decision whether the low experimental value is correct can therefore only be made with calculations for substituted compounds. To date, only NDDO-type semiempirical calculations have been performed for substituted compounds.[33] These methods show shortcomings in the description of four-membered rings present in the Dewar forms, so it is questionable whether they can give definite results for ΔH_R.

By use of sophisticated ab initio methods, our calculations on the substituted compounds should yield reliable data for the isomerization energies and, furthermore, should show the trends due to various substituents. In particular they should help to determine whether the discrepancy between calculated and measured ΔH_R for substituted [6]paracyclophanes is due to shortcomings in the theoretical treatment or whether it is more likely that experiments need reevaluation.

2. Technical Details

Self-consistent field (SCF) theory using various Gaussian basis sets[34] (see Table 1) of split valence (SV), double-ζ plus polarization (DZP) and triple-ζ plus polarization (TZP) quality was used for the investigation of the molecules listed in Table 2 and Figure 1.

Complete geometry optimizations of all geometrical parameters were performed with the SV and DZP basis sets. If the symmetry of the molecule was not known before with certainty, the first optimization run was performed with the SV basis without any symmetry constraints in order to determine the structure with the lowest energy. The symmetries found in this way are given in Table 2. The geometries were subsequently optimized with the DZP basis set. For the largest compounds, 1,2-dicarbethoxy-3,6-dimethylbenzene and 8,9-dicarbethoxy[6]paracyclophane, geometry optimizations were carried out only with the SV basis set.

The geometries obtained with the SV basis set do not significantly differ from those obtained with the DZP basis set. The differences in the bond lengths are less than 0.01 Å, those of the bond angles less than 1°. Thus, it is concluded that there is no necessity to use even larger basis sets for geometry optimizations, which has been recognized before for [4]paracyclophane.[32]

The SV, DZP, and TZP basis sets were used to calculate initial values for the energy difference between the two isomers. The correlation energy contributions to the isomerization energies were calculated by second-order Møller–Plesset perturbation theory (MP2) with the 1s orbitals of the second-row atoms frozen. The zero-point-energy (ZPE) corrections were calculated in the harmonic approximation. The calculations and geometry optimizations were carried out with the TURBOMOLE program package.[35,36] The MP2 calculation for DC[6]P and its Dewar form was done using the FullDirect method of the Gaussian 92 program package[37] since it afforded too much disk space to be done in the conventional way.

The differences between the reaction enthalpies at 0 K and those at room temperature were estimated for benzene and [6]paracyclophane. According to these results, this amount should be lower than 0.5 kcal/mol and is therefore neglected (that is, our calculated quantity is $\Delta H_R \approx \Delta E_{SCF/MP2} + \Delta E_{ZPE}$).

3. Results and Discussion

3.1. Geometry. The geometries of benzene, HFB, HMB, and [6]paracyclophane as well as the geometries of Dewar benzene and [6]Dewar benzene have previously been studied by ab initio methods.[3,4,38–40] For our purposes the steric interaction between substituents is of importance. As can be seen from Figure 2, in which HMB is given as an example, the methyl groups of the benzene form are significantly closer to each other than those of the corresponding Dewar form, so that the steric interaction of substituents in the benzene form is greater (shortest C–C distance: HMB, 2.917 Å; HMDB, 3.435 Å; shortest H–H distance: HMB, 2.168 Å; HMDB, 2.573 Å).

The rings of HMB and PFHMB are not strictly planar due to these steric interactions; the dihedral angles between four directly connected ring atoms are 3° and 6.5°, respectively. For HMB,

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Table 2. Compounds Investigated in the Present Work[a]

name	abbreviation	substituents	symmetry	
			benzene	Dewar
benzene		$R_1 = R_2 = R_3 = H$	D_{6h}	C_{2v}
hexafluorobenzene	HFB	$R_1 = R_2 = R_3 = F$	D_{6h}	C_{2v}
1,4-dimethylbenzene	p-DMB	$R_1 = CH_3, R_2 = R_3 = H$	C_{2h}	C_{2v}
1,2,3,4-tetramethylbenzene	TMB	$R_1 = R_2 = CH_3, R_3 = H$	C_2	C_s
hexamethylbenzene	HMB	$R_1 = R_2 = R_3 = CH_3$	D_{3d}	C_{2v}
perfluorohexamethylbenzene	PFHMB	$R_1 = R_2 = R_3 = CF_3$	C_3	C_2
1,2-dicarbethoxy-3,6-dimethylbenzene	DCDMB	$R_1 = CH_3, R_2 = COOC_2H_5, R_3 = H$	C_2	C_1
[6]paracyclophane	[6]P	$R_1 = H$	C_2	C_2
8,9-dimethyl[6]paracyclophane	DM[6]P	$R_1 = CH_3$	C_1	C_1
8,9-dicarbethoxy[6]paracyclophane	DC[6]P	$R_1 = COOC_2H_5$	C_1	C_1

[a] The general structure is given in Figure 1. Abbreviations used in the text and the symmetries of the compounds are also given.

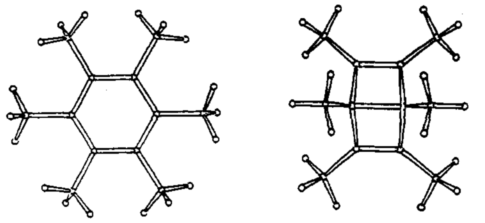

Figure 2. Geometries of HMB and its Dewar form. In the benzene form the methyl groups are significantly closer to each other. Shortest C–C distance: HMB, 2.917 Å; HMDB, 3.435 Å. Shortest H–H distance: HMB, 2.168 Å; HMDB, 2.573 Å.

Table 3. Selected SCF-Calculated Geometry Data for the Paracyclophanes[a]

compound	basis set	r_1 (Å)	r_2 (Å)	ϕ (deg)	α (deg)	β (deg)
			Benzene Forms			
[6]P	SV	2.766	2.392	158.3	18.4	21.1
	DZP	2.749	2.375	158.2	18.5	21.1
DM[6]P	SV	2.753	2.407	157.5	19.4	20.2
	DZP	2.736	2.391	157.4	19.5	20.3
DC[6]P	SV	1.766	2.391	156.6	19.9	19.6
			Dewar Forms			
[6]P	SV	1.601	2.584	114.6	80.9	28.1
	DZP	1.573	2.567	114.8	81.3	28.4
DM[6]P	SV	1.592	2.585	114.5	81.3	28.4
	DZP	1.568	2.568	114.7	81.5	28.8
DC[6]P	SV	1.595	2.571	113.9	81.2	28.4

[a] The notation is defined in Figure 3.

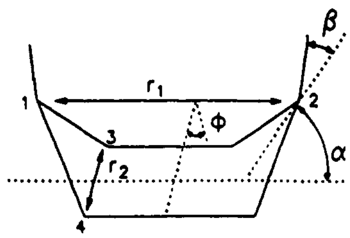

Figure 3. Definition of the geometrical parameters of the [6]paracyclophanes.

the structure with D_{3d} symmetry has been found to be the most stable one, in agreement with previous calculations.[38] In PFHMB the greater steric interaction of the CF_3 groups causes a lower symmetry (C_3).

Table 3 lists the relevant geometrical data for the bridged compounds. The definitions of r_1, r_2, ϕ, α, and β are depicted in Figure 3. It can be seen by inspection that the geomery of the ring system changes only very slightly if substitution takes place at the ring. The values of r_1 and r_2 differ by less than 0.03 Å, those for ϕ, α, and β by less than 2°.

Our values for the deformation angle α agree well with the experimental values, as can be seen from Table 4, in which other theoretical data are also given for comparison.

Table 4. Comparison of the Calculated Value of the Deformation Angle α (in deg, See Figure 3) of the [6]Paracyclophanes with Other Theoretical and Experimental Data[a]

	α			
method	[6]P	DM[6]P	DC[6]P	ref
SCF, SV	18.4	19.4	19.9	present work
SCF, DZP	18.5			present work
SCF, DZ	18.6			41, 25
MNDO	25.3			42
AM1	22.8	23.2		33
MM	22.4			43
MM	22.8			44
exp		20.5	19.5	20, 45

[a] The first three rows contain SCF calculations with different AO basis sets; the following rows refer to the results of semiempirical MNDO and AM1 calculations, while MM refers to molecular mechanics calculations.

3.2. Isomerization Enthalpies. The calculations of the energy differences with the TZP basis were carried out at the DZP optimized structures. The energy differences ($\Delta E = E_{\mathrm{Dewar}} - E_{\mathrm{Benzene}}$) at the SCF level of theory (ΔE_{SCF}), the differences of the MP2 energy corrections (ΔE_{MP2}), and the differences in the zero-point energies (ΔE_{ZPE}) are collected in Table 5. Inspection of these values shows that the energy difference between the benzene and Dewar form at the SCF level decreases significantly by inclusion of d-polarization functions (SV vs DZP). This is due to the fact that the polarization functions are more important for the description of the strained four-membered ring in the Dewar form. Therefore, in contrast to our findings for the determination of the geometries, the SV basis set is not large enough for the reliable calculation of the enthalpies. The DZP values agree with those calculated with the TZP basis set to within 1 kcal/mol (with the exception of the fluorinated compounds); thus, it can be assumed that our best values for ΔE_{SCF} are within 1 kcal/mol of the spd basis set limit. Furthermore, f functions do not contribute significantly to ΔE_{SCF} (see Table 6), so that our values can be regarded to be near the Hartree–Fock limit.

For the unbridged compounds, the MP2 contributions decrease the energy difference between the two forms significantly; that is, the correlation energy of the Dewar form is greater. The reverse trend is found for the [6]paracyclophane molecules, in which the deformation of the aromatic ring induces a stronger admixture of ionic (doubly substituted) configurations, which in turn lowers the correlation energy. The calculations of Grimme[32] on [4]paracyclophane isomers have shown that there is little difference between the isomerization enthalpies calculated with MP2 and MRD-CI correlation treatments. The unsubstituted [6]paracyclophane isomers have been investigated using MRD-CI by Arnim et al.[4] (see Table 6). These results for [6]P differ from the results of our SCF/MP2 calculations by about 10 kcal/mol. When comparing the MP2 and MRD-CI results, one must consider that the system is very large so that the MRD-CI

Table 5. Differences of the SCF Total Energies ΔE_{SCF}, MP2 Corrections ΔE_{MP2}, and Zero-Point Energies ΔE_{ZPE} between the Dewar Benzene and Benzene Form (in kcal/mol)

compound	basis set	ΔE_{SCF}	ΔE_{MP2}	ΔE_{ZPE}	ΔE_{tot}	ΔH_R(exp)
benzene	SV	102.0	−11.4	−1.9	88.7	
	DZP	87.8	−6.3	−1.5	79.9	
	TZP	87.5	−7.4	−1.5	78.6	
HFB	SV	85.3	−10.4	0.2	75.1	
	DZP	68.2	−4.3	0.2[a]	64.1	
	TZP	64.9	−4.5	0.2[a]	60.6	
p-DMB	SV	98.6	−12.4	−1.6	84.7	
	DZP	85.0	−7.5	−1.6[a]	75.9	
	TZP	85.2	−8.8	−1.6[a]	74.8	
TMB	SV	86.0	−9.0	−2.3	74.8	
	DZP	72.5	−3.6	−2.3[a]	66.6	
	TZP	73.2	−5.1	−2.3[a]	65.8	
HMB	SV	68.8	−4.0	−2.6	62.3	56–60[b]
	DZP	55.6	1.4	−2.6[a]	54.4	
	TZP	56.9	−0.1[a]	−2.6[a]	54.2	
PFHMB	SV	32.0	−1.9			28[c]
	DZP	24.5				
	TZP	22.0				
DCDMB	SV	88.5	−6.3	−2.3[a]	79.9	
	DZP	75.3	−0.9[a]	−2.3[a]	72.1	
	TZP	74.7	−2.4[a]	−2.3[a]	70.0	
[6]P	SV	57.5	1.3	−1.5	57.2	
	DZP	45.1	5.0	−1.5[a]	48.6	
	TZP	45.7	3.7[a]	−1.5[a]	47.9	
DM[6]P	SV	45.6	5.8	−2.2[a]	49.2	
	DZP	33.2	11.2[a]	−2.2[a]	42.2	
	TZP	34.0	9.7[a]	−2.2[a]	41.5	
DC[6]P	SV	48.0	8.3	−2.2[a]	54.3	5.6[d]
	DZP	35.8	13.7[a]	−2.2[a]	47.3	
	TZP	35.0	12.2[a]	−2.2[a]	45.0	

[a] Estimated from the values for smaller basis sets and analogous compounds (see text). [b] References 11–13. [c] Reference 15. [d] Reference 28 (in *o*-xylol).

Table 6. Comparison of the Energy Differences (without ZPE Corrections) between the Dewar Benzene and Benzene Form with Other Theoretical Values (All Values in kcal/mol)

	ΔE		
method/basis set	benzene	[6]paracyclophane	ref
SCF, SV/MP2	90.6	58.8	present work
SCF, DZP/MP2	81.5	50.1	present work
SCF, TZP/MP2	80.1	49.4	present work
SCF, DZ2P/MP2	82.3		4
SCF, TZ2P/MP2	80.5		4
SCF, TZ2P+D/F/MP2	80.3		4
MCPF	75.9–78.0	37.5–37.7	4
MRD-CI	79.6–81.2	39.3	4
CAS-SCF	82.3	43.0	4

calculations[4] correlated only 20 electrons in a canonical MO basis and were therefore not able to account for the entire correlation energy difference of the two systems. On the other hand, we can also not exclude that the MP2 values for the [6]paracyclophanes may be 5–10 kcal/mol too high.

For the larger molecules and basis sets some of the MP2 calculations could not be performed due to limited storage capacities. In these cases, the values were estimated according to the corresponding values obtained for the unbridged compounds (for a detailed explanation see below).

The highest isomerization energy is found for benzene itself (79 kcal/mol). Generally, substitution of the ring results in a reduction of the ΔE values. The substitution effects seem to be nearly additive (see below), so that low values compared to benzene are found for HFB (61 kcal/mol), HMB (54 kcal/mol), and PFHMB (22 kcal/mol at the SCF level). In summary, we find a lower energy difference as well for substitution by CH_3 (electron donor) as well as by F (σ acceptor, π donor), and CF_3 (electron acceptor).

Furthermore, it must be mentioned that steric effects have to be considered, too. With fluorine as a substituent, steric interactions should be negligible since the van der Waals radii of the F atoms in an ortho arrangement do not overlap.[39] In the case of methyl substituents, the interaction of ortho-substituted methyl groups should have a larger influence on the enthalpy. To allow for comparison with a compound in which no steric interactions are possible, we have calculated the isomerization enthalpy for p-DMB. Here we find an energy difference that is 4 kcal/mol lower than that for benzene. Extrapolation of this difference for an estimation of the isomerization enthalpies for TMB and HMB yields values which are too large. This demonstrates that the steric interaction in the benzene forms is greater. Due to this steric contribution, the lowering of the enthalpy by four or six methyl groups is not equal to the difference between the values for benzene and p-DMB. From the calculated values this contribution can be estimated to be about 5 kcal/mol for TMB and 13 kcal/mol for HMB. Of course, these values are not exact since the effects are not purely additive and the positions of the methyl groups in the Dewar form are not equivalent.

Another way to obtain estimated values for the steric energies in TMB and HMB is to calculate the energies of homodesmic reactions such as 3 p-DMB → HMB + 2 benzene and 2 p-DMB → TMB + benzene. These reaction energies can be easily obtained using our calculated total energies in Table 5. The values found in this way for the steric energies are similar to those given above (within 2 kcal/mol for TMB and about 4 kcal/mol for HMB).

An interesting correlation can be shown by subtracting the ΔE values of the [6]paracyclopanes from those of the corresponding substituted benzenes. The differences obtained in this way are the same for the three pairs p-DMB − [6]P, TMB − DM[6]P, and DCDMB − DC[6]P with a deviation of ≤1.8 kcal/mol for the total energies and ≤1.1 kcal/mol for the differences between benzene and Dewar forms (Table 7). Of course, a certain correlation is expected, but the good numerical agreement of the values is surprising.

We used this correlation to estimate some of the values which we could not calculate. For example, the MP2 contribution to ΔE for DM[6]P at the TZP level was estimated using the SV/MP2 value and the difference $\Delta E_{TZP/MP2} - \Delta E_{SV/MP2}$ found for TMB. This approximation seems reasonable, since the basis set dependence of the MP2 contributions to ΔE varies only slightly for different molecules. The zero-point energy of DM[6]P was estimated using the corresponding ΔE_{ZPE} value for [6]P and the difference ΔE_{ZPE}(TMB) − ΔE_{ZPE}(p-DMB).

Obviously, it is possible to estimate the isomerization enthalpy of [6]paracyclophanes by subtraction of a certain amount from the isomerization enthalpy of the corresponding substituted benzene. According to our calculations with the TZP basis set, this amount is 39.5 ± 0.5 kcal/mol at the SCF level without any further corrections. This energy difference can be interpreted as the strain energy of the [6]paracyclophane ring which is set free during the isomerization reaction. Due to the stronger electron correlation in the benzene forms, the corresponding value including MP2 corrections is lower by 12–15 kcal/mol.

The correlation between the isomerization enthalpies of the [6]paracyclophanes and the benzenes can be interpreted as a further argument for the aromaticity of the [6]paracyclophanes. They are obviously influenced by substitution in just the same way as normal, planar aromatic systems. This has been investigated for only three systems, but for the other [6]paracyclophanes prepared up to date, such as 8,9-bis((*N*-phenylcarbamoyl)methyl)[6]paracyclophane, 8,9-bis((*N*-cyclohexylcarbamoyl)methyl)[6]paracyclophane, or 8,9-bis(acetoxymethyl)[6]paracyclophane,[27,28,33] we expect a similar correlation

Table 7. Energy Differences between the [6]Paracyclophanes and the Corresponding Benzenes (in kcal/mol)[a]

compound	basis set	δE_{SCF} benz. (au)	δE_{SCF} Dew. (au)	$\Delta\delta E_{SCF}$ (kcal/mol)	δE_{MP2} benz. (au)	δE_{MP2} Dew. (au)	$\Delta\delta E_{MP2}$ (kcal/mol)
[6]P	SV	154.7016	154.7671	41.1	0.3817	0.3600	−13.6
	DZP	154.8898	154.9533	39.8	0.5852	0.5654	−12.4
	TZP	154.9359	154.9987	39.4			
DM[6]P	SV	154.7025	154.7671	40.5	0.3845	0.3610	−14.7
	DZP	154.8906	154.9532	39.3			
	TZP	154.9362	154.9986	39.2			
DC[6]P	SV	154.7027	154.7673	40.5	0.3848	0.3615	−14.6
	DZP	154.8904	154.9534	39.5			
	TZP	154.9352	154.9986	39.8			

[a] δE_{SCF}: differences of the calculated total SCF energies. $\Delta\delta E_{SCF}$: differences of the calculated ΔE_{SCF} values.

since the substituents employed should have similar inductive and mesomeric effects as those of the theoretically investigated molecules.

The calculated ΔE value of HMB (54 kcal/mol) is in good agreement with the experimentally measured reaction enthalpy ΔH_R (58–60 kcal/mol[11-13]). The assumption found in the literature[3,14] that this value should be a good estimate of the unknown reaction enthalpy of benzene cannot be substantiated. According to our calculations, there is a large difference between the two values of about 25 kcal/mol.

In addition, the calculated value for PFHMB (22 kcal/mol at the SCF level) agrees well with the experimental value of 28 ± 1 kcal/mol.[15] This very small energy difference between the benzene and Dewar forms is mainly attributed to the strong deformation of the benzene ring (see 3.1) which is caused by the interactions of the quite large CF_3 groups. The electronic effect on the isomerization enthalpy should not be significantly larger than that in HFB.

With the exception of PFHMB the isomerization enthalpies found for the [6]paracyclophanes are generally much smaller than those found for the compounds without the $(CH_2)_6$ chain. However, the ΔE values are still about 40 kcal/mol higher than the experimental value for DC[6]P (5.6 kcal/mol[28]). Since the calculated values for HMB and PFHMB show good agreement with experiment (they even tend to be a bit lower than the experimental data), we conclude that the calculations account well for substitutent effects and presume that the experimental value for DC[6]P is too low.

However, it has to be mentioned that the measurement for DC[6]P has been done in a calorimeter with *o*-xylol as solvent, while the calculated values refer to gas phase. The interaction with the solvent may cause a shift of the experimental ΔH_R values, but we do not think it is likely that solvent effects account for more than several kilocalories/mole to ΔH_R.

4. Conclusions

The results of our ab initio calculations show that the benzene form is destabilized relative to the Dewar form by substitution with both electron acceptors and electron donors. The trend of the reaction enthalpies in the series p-DMB, TMB, and HMB can be explained by an additional steric effect which destabilizes the benzene form relative to the Dewar form. The isomerization enthalpy of HMB is found to be 25 kcal/mol lower than that of benzene. This shows that it is not justifiable to estimate the value for benzene from the experimental value for HMB.

Our results for HMB and PFHMB are in good agreement with the experimental data.[11-13,15] Furthermore, the small changes when going from DZP/MP2 to TZP/MP2 suggest that for the present purposes calculations using larger basis sets are not required. Our results at the TZP/MP2 levels seem reliable, and we feel that the large deviation from the experimental value for DC[6]P[28] is due to experimental uncertainties.

We can show a correlation between the energies of the [6]-paracyclophanes and the corresponding substituted benzenes which allows the isomerization enthalpy of the [6]paracyclophanes to be estimated from the values of the unbridged benzenes. This is interpreted as a further argument for the aromaticity of these nonplanar systems.

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Note added in proof. The ΔH_R values of substituted [6]paracyclophanes have recently been redetermined by Dreeskamp et al. (private communication). An improved experimental method gave a significantly larger ΔH_R value for DC[6]P (to be published) which is in better agreement with the MP2 value of 45 kcal/mol.