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Ab initio study of the stability of [*n*]paracyclophanes and their Dewar benzene-type isomers*

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Summary. *Ab initio* calculations are carried out for [*n*]paracyclophanes and their Dewar benzene isomers for $n = 5$, 6, and 7 as well as for the benzene and Dewar benzene itself. The benzene isomers are studied by employing various AO basis sets ranging from 6-31G type to such of triple-zeta type including two *d* and one *f* function on the carbons and two *p* and one *d* on the hydrogens. The correlation energy contribution is computed by employing MP2, CAS-SCF, MRD-CI and MCPF procedures. Potential curves for the low-energy states in the isomerization from benzene to its Dewar form are also computed under certain geometrical assumptions. The energy difference between the two potential minima is calculated to be 3.35 eV; neglect of electron correlation increases the value by about 0.3 eV, deficiencies in the polarization description (6-31G basis) overestimates it by another 0.65 eV. The calculations suggest that the experimental Dewar benzene geometry determination needs refinement and that the isomerization energy of hexamethylbenzene is considerably smaller than that of benzene itself.

The geometries of the [*n*]paracyclophanes in both isomer forms are optimized in the 6-31G basis; the energy difference is determined by employing an AO basis of double-zeta quality plus polarization functions. Correlation effects are considered. The electronic isomerization energies are 2.58 eV ($n = 7$), 1.63 eV ($n = 6$) and 0.7 eV ($n = 5$) for the unsubstituted compounds. The relative energetics are discussed in terms of potential surface diagram having the benzene ring deformation as the "reaction coordinate". Comparison with the anthracene isomerization is made and the effect of substituents is pointed out.

Key words: [*n*]-Paracyclophanes – Dewar benzene isomers

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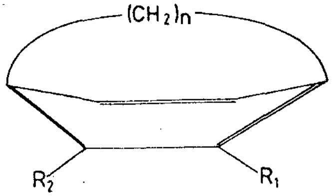
* Dedicated to Alberte Pullman

1. Introduction

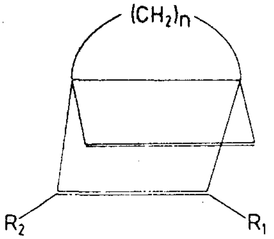
The family of [*n*]paracyclophanes (1)



(1)

has received considerable attention over the past decades [1, 2]. Depending on the length of the CH_2 chain (the value of n) the benzene ring is more or less deformed away from its planarity, and the strain energy of the total system increases with decreasing n. The interesting question arises how much strain the benzene ring is able to tolerate in such systems, i.e. how short the $(CH_2)_n$ chain can become, and furthermore, to what extent substitutions on the bezene ring are able to favor the deformations. The first synthesis was achieved for $n = 10$ about 40 years ago [3], whereas the compound [5]paracyclophane was synthesized as late as 1985 [4]. In the discussion of molecular properties, the question, whether the [*n*]paracyclophanes maintain for small n the aromaticity of the benzene ring or not led to considerably controversy [4–7].

The photochemical behavior of [*n*]paracyclophanes is of particular interest. [6]paracyclophane has been found [8] to show photochemical interconversion to its Dewar benzene isomer (2).



(2)

This valence isomerization has also been observed for [6]paracyclophanes with various substituents on the benzene ring [9–12]. Irradiation of disubstituted [6]paracyclophane (with $R = COOC_2H_5$, for example) with wavelength of 310 nm has been found to produce the Dewar-type isomer with a quantum yield of 0.024; the reverse photoreaction occurs upon excitation with 288 nm and a quantum yield of 0.12 [10]. The thermal back reaction from the Dewar-type isomer to the aromatic compound has been found to occur quantitative with an Arrhenius parameter of $E_a = 88$ kJ/mole and $\log A = 9.3$; the reaction enthalpy was measured as $\Delta H = -19.8$ kJ/mole [10]. On the other hand, [5]paracyclophane and various derivatives have been produced via photochemical reactions starting with the Dewar-type compound [4, 13, 14].

From the various photochemical experiments it has been concluded that [*n*]paracyclophanes can be divided into three groups: for $n > 6$ the Dewar isomers are not formed photochemically. [*n*]paracyclophanes for $n < 4$ have not been synthesized yet but there is evidence that only the corresponding Dewar isomer exists [15] since experiments to transform it into its benzene-like form have not yet been successful. The system for $n = 4$ with substituents is also known in its Dewar form [16, 17]. The most interesting group is those for $n = 5$ and $n = 6$ since [6]paracyclophane (at least in the substituted form) occurs in both isomer forms, whereby the aromatic form is thermodynamically stable; there is indication that for [5]paracyclophanes the Dewar isomer is energetically the preferred species [10], at least in the substituted form.

Most theoretical treatments have dealt only with the benzene-like isomer. The majority of them are semiempirical in nature, making use of MNDO [18] or AM1 [12, 18], force field or molecular mechanics procedures [12, 19, 20] and concentrate on the determination of the molecular geometry, the strain energy and the question of aromaticity. It is noteworthy that for the $(CH_2)_n$ bridge with odd n there are always three possible lower-energy structures: two of C_2 symmetry with the middle CH_2 "up" or "down" [20] and one of C_s conformation, while for even n only one type of the $(CH)_n$ arrangement is important. The only *ab initio* work to our knowledge is that by Rice, Lee et al. [5, 6] and Remington et al. [21] for [5]paracyclophane, [6]paracyclophane and [7]paracyclophane, in which the geometry is optimized in an SCF treatment employing an AO basis set at the STO-3G [21] and DZ [5, 6] level. An *ab initio* study of the benzene isomerization has been undertaken in a 4-31G AO basis set [22].

In our present theoretical study we want to concentrate on the benzene-like and Dewar benzene-like isomers for the interesting [*n*]paracyclophanes with $n = 5$, 6 and 7, for which according to experimental evidence the Dewar form seems to be preferred for $n = 5$, detailed experimental data are available for the isomerization process of the system with $n = 6$ while the interconversion to the Dewar form has not been achieved for the $n = 7$ compound. We will employ *ab initio* methods for this study. Since an SCF treatment is generally not sufficient for the study of relative energies/stabilities, the correlation energy contribution will also be estimated and various levels of a theoretical approach will be employed for this purpose. Various AO basis sets will also be used in the study in order to estimate the AO basis set influence on the reliability of results. Finally, comparison will be made with the two isomers corresponding to $n = \infty$, namely benzene itself and Dewar benzene. The goal thereby is to obtain a more general understanding of the electronic structure and the relative energetics of the various isomers with different length of the $(CH_2)_n$ bridge, and in comparison with experiment, obtain possibly some information on effects of substituents on this situation.

2. Technical details

The obvious *ab initio* treatment for the various [*n*]paracyclophanes would be one which employs a large AO basis set and correlated wavefunctions for the entire multidimensional potential energy surface connecting the aromatic and Dewar benzene-like isomers, including optimization of all geometrical variables to

Table 1. Summary of AO basis sets employed

Notation		Description[a]	Reference
6-31G	C:	$(10s, 4p) \rightarrow [3s, 2p]$	[b]
	H:	$(4s) \rightarrow [2s]$	
DZ + D	C:	$(9s, 5p) \rightarrow [4s, 2p]$ plus $d(0.60)$	[48]
	H:	$(4s) \rightarrow [2s]$ scaling factor $\eta^2 = 2.0$	[29]
DZ + 2D	as DZ	plus 2 × $d(0.46, 1.39)$	
DZP	C:	$(8s, 4p) \rightarrow [4s, 2p]$ plus $d(0.8)$	[c]
	H:	$(4s) \rightarrow [2s]$ plus $p(0.8)$	
DZ2P	C:	$(8s, 4p) \rightarrow [4s, 2p]$ plus 2 × $d(0.46, 1.39)$	[c]
	H:	$(4s) \rightarrow [2s]$ plus 2 × $p(0.46, 1.39)$	
TZ2P	C:	$(9s, 5p) \rightarrow [5s, 3p]$ plus 2 × $d(0.46, 1.39)$	
	H:	$(5s) \rightarrow [3s]$ plus 2 × $p[0.46, 1.39]$	
TZ2P + D/F	as TZ2P	plus $d(0.8)$ on H plus $f(0.6)$ on C	

[a] The notation $(i, j) \rightarrow [k, l]$ refers in the standard manner to i primitive s and j primitive Gaussian p functions contracted to k Gaussian s groups and l Gaussian p groups

[b] From HONDO basis set library, originally Ref. [47]

[c] From the TURBOMOLE-library; generally carbon functions from Ref. [48], hydrogens from Ref. [29]

obtain the minimum energy path. Since this is beyond our computer capacity we have attempted to employ for a given calculation as much computational and theoretical effort as felt necessary to obtain chemically meaningful results, still staying with our budget. Therefore a hierarchy of AO basis sets and treatments is employed at various points and we will discuss these each time in connection with the results. A list of the various AO basis sets including a short description is contained in Table 1.

SCF calculations are generally carried out by employing the TURBOMOLE program package [23] which also allows to estimate the correlation energy contribution in second-order Møller–Plesset (MP2) perturbation theory. Multireference configuration interaction calculations (MRD-CI) are undertaken in our standard manner [24]: the most important configurations of the MRD-CI space are treated variationally (selected) while the energy contribution of the unselected species is taken into account in a more global manner [25]. Estimates of the full CI energy are made in analogy to the Davidson correction [26, 27].

3. Isomerization of benzene and Dewar benzene

3.1. Potential energy surfaces

In order to obtain an idea of the approximate potential surface relating the two isomers, a series of calculations was carried out in the following manner:

The geometry for the two isomers benzene ($R_{CC} = 1.4$ Å, $R_{CH} = 1.08$ Å) and Dewar benzene [28] was taken from the literature. The deformation angle α (or equivalently ϕ) was chosen as "reaction coordinate" (Fig. 1), i.e., seven values including the end points $\alpha = 0$ (benzene) and $\alpha = 81°$ (Dewar benzene); all other structural parameters were changed in a linear manner between the values of the end points. This is certainly an approximation, and for a more quantitative determination of the minimum energy path in ground and excited states an optimization of at least the most important geometrical variables would be required.

The AO basis was smaller than all those of Table 1. It consists of the original three *s* hydrogen basis of Huzinaga [29] contracted to one function, scaled by a factor of $\eta^2 = 2.0$ and the four *s* and four *p* Gaussian functions for carbon [30] in the contraction to two *s* and two *p* groups (shorthand notation [2*s*, 2*p*]). The 1*s* of carbon is described by a pseudopotential derived by Durand and Barthelat [30, 31].

SCF and MRD-CI calculations are carried out for each geometry for various electronic states; the canonical MO's of the $^1A_1$ ground state were employed as orbital basis in the CI step and 14 electrons were correlated, i.e., a core of the lowest-lying three a_1, two b_1, two b_2 and one a_2 valence MO was always kept doubly occupied. A few technical details are contained in Table 2.

The orbital correlation diagram for the highest occupied and the lowest unoccupied MO's is displayed in Fig. 2 while the corresponding potential energy curves are collected in Fig. 3. A similar orbital diagram is found in Ref. [32].

The change in orbital stability from benzene to Dewar benzene is obvious from the overlap-consideration of the atomic function, indicated in the figure as the largest contributor to the individual MO's. The prominent feature is the stability loss of one of the $e_{1g}(b_1)$ components and the stabilization of the $e_{2u}(a_1)$ component. This orbital crossing occurs between $\alpha = 45°$ and 55° and manifests itself in the barrier of the ground state potential surface as seen in Fig. 3. The complementary A_1 state in this avoided crossing is also calculated, and it is

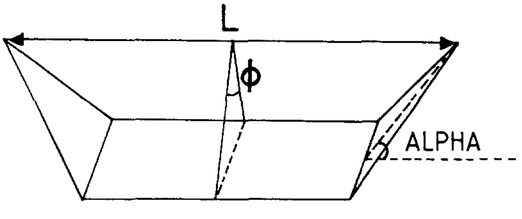


Fig. 1. Definition of the pertinent geometrical parameters employed in the present work

Table 2. Selected technical details for the potential curve calculations in Fig. 3[a]

State[b]	Reference configs.	Total number of SAF's	Average selected number of SAF's	$\sum c^2$ %
$^1A_1(^1A_{1g}, {}^1E_{2g})$	29	890312	13000	91-88
$^3B_1(^3B_{1u})$	17	1192208	14000	91-90
$^1B_2(^3B_{2u})$	12	463608	11000	91-87
$^1B_1(^1B_{1u})$	14	449613	14000	90-88

[a] Given are the number of reference configurations for the MRD-CI treatment, the total number of symmetry-adapted functions (SAF) in the MRD-CI space, the average number of SAF explicitly treated in the secular equation (selected SAF) and the contribution of the reference configurations to the total MRD-CI expansion on the basis of their coefficients

[b] For the $^1A_1$ state three roots are calculated for $\alpha = 0.0°$, 13.5, 27.0°

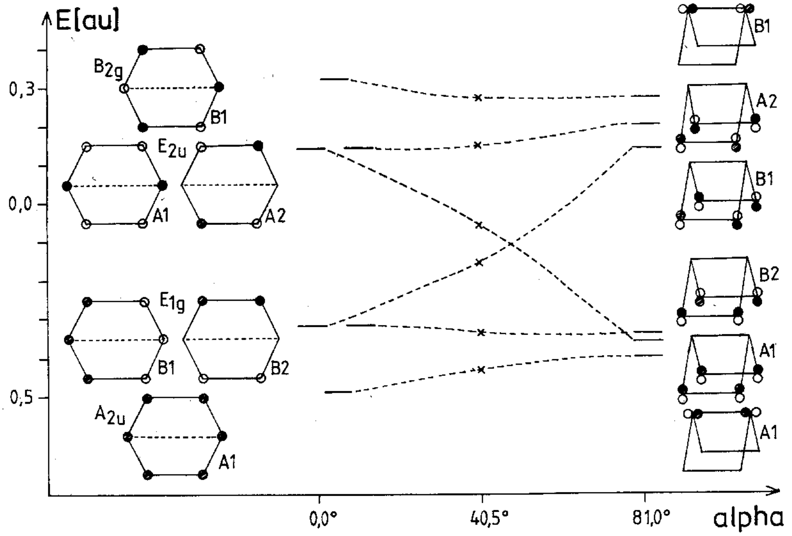


Fig. 2. Orbital energy diagram for the isomerization from benzene to Dewar benzene

connected with the $^1E_{2g}$ state of benzene only via another barrier due to the avoided crossing with a third state of this $^1A_1$ symmetry.

The lowest triplet benzene state $^3B_{1u}$–$^3B_1$ lies above the X^1A_1 state in the entire isomerization area. The singlet states interact with each other in a similar manner as shown by Meisel and Janoschek [22].

Since the AO basis set is relatively poor in these investigations, and geometry optimization has not been undertaken, the results of Fig. 3 should be considered to be only qualitatively but not quantitatively correct. The errors on the benzene side can obviously be given simply by comparing the calculated and measured excitation energies: $^3B_{1u}$ 4.3 eV instead of 3.9 eV, $^1B_{2u}$ 5.4 eV instead of 4.9–5.0 eV and $^1B_{1u} = 7.4$ eV instead of 6.2–6.3 eV; the latter discrepancy is not surprising since it is known that more diffuse AO basis functions than are present in the AO basis employed are required for a proper description of the $^1B_{1u}$ state.

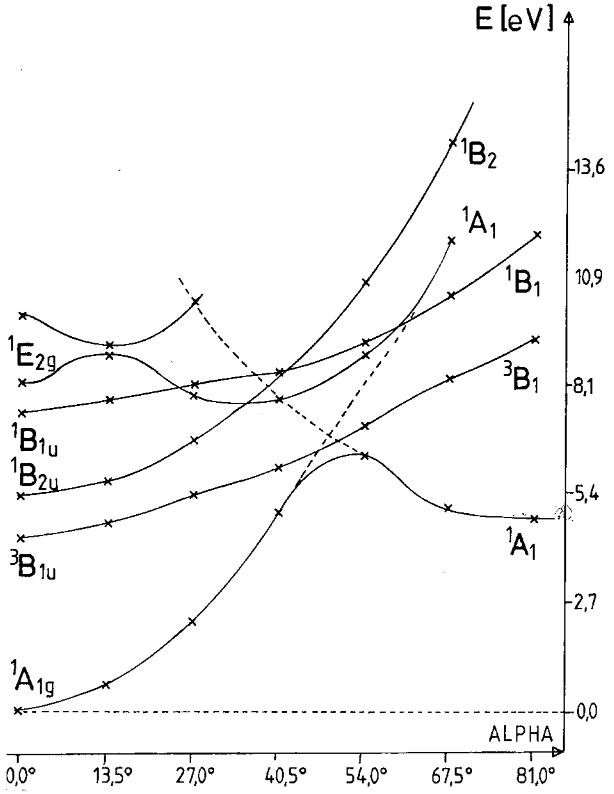


Fig. 3. Calculated potential energy curves for the isomerization between benzene and Dewar benzene

3.2. The relative stability between benzene and its Dewar isomer

SCF and MP2 calculations are carried out for benzene and Dewar benzene in their respective equilibrium structure in order to estimate the influence of the atomic orbital basis. The results are summarized in Table 3.

It is seen that the isomerization energy at the SCF level ΔE_{SCF} varies by not more than 0.2 eV by employing AO basis sets of different size, provided they are at least of double-zeta quality including some polarization functions. It is furthermore seen, that the correlation energy contribution, as evaluated by the MP2 procedure, is larger for the Dewar form than for the aromatic form by about 0.25 eV. As a consequence all isomerization energies calculated at the MP2 level are lower than those of the SCF treatment by just this amount. This is not unusual, since it has been found for various other isomers that the correlation energy error is larger in the more strained system than in the open-chain-analogue. The absolute magnitude of the correlation energy accounted for increases, of course, with the size of the AO basis set for both isomers.

The next question is, whether the perturbation treatment MP2 is sufficient to account for the correlation energy difference between the two benzene isomers. Therefore, a number of other treatments are undertaken, as summarized in Table 4. The complete-active space (CAS)-SCF [33] allowing six electrons in the six orbitals sketched in Fig. 2 is the least extensive of the correlation treatments, and as such accounts for the smallest amount of correlation energy. If 30 electrons are correlated, as in the multiconfigurational pair function (MCPF) treatment

Table 3. Calculated energies for the difference of benzene and Dewar benzene (isomerization energies) as obtained from various AO basis sets (see Table 1) employing the SCF and MP2 treatment[a]

AO Basis	ΔE_{SCF} (eV)	ΔE_{MP2} (eV)	E_{corr} (Benzol) (a.u.)	E_{corr} (Dewar) (a.u.)	ΔE_{corr} (eV)
6-31G	4.35	—	—	—	—
DZ + D	3.64	—	—	—	—
DZ + 2D	3.67	—	—	—	—
DZP	3.82	3.53	.7833	.7937	.28
DZ2P	3.73	3.58	.8354	.8412	.16
TZ2P	3.72	3.50	.8719	.8800	.22
TZ2P + D/F	3.76	3.49	.9436	.9535	.27

[a] ΔE refers to the isomerization energy, E_{corr} to the amount of correlation energy accounted for in the MP2 treatment for the two isomers, and ΔE_{corr} is the correlation energy difference between the Dewar and aromatic benzene isomer.

For Dewar benzene the 6-31G optimized geometry has been employed

Table 4. Calculated isomerization energies ΔE_{iso} and correlation energy contributions for benzene and Dewar benzene as obtained from different correlation treatments

Type of treatment	ΔE_e (eV)	E_{corr} (a.u.) Benzene	E_{corr} (a.u.) Dewar	ΔE_{corr} (eV)
MCPF, 30*e* DZ + D Basis, canon . MO 1*s* in core	3.30	0.7912	0.8038	0.34
MCPF, 30*e* DZ + 2D Basis, canon. MO 1*s* in core	3.39	0.8343	0.8448	0.29
MCPF, 18*e* DZ + D Basis, LMO 1*s* Plus CH bonds in core	3.35	0.4499	0.4605	0.29
MRD-CI, 18*e* DZ + D Basis, CAS-MO 1*s* plus CH bonds in core	3.53	0.4480	0.4520	0.11
MRD-CI, 20*e* DZ + D Basis, canon. MO MO with $\epsilon < -0.8$ a.u. in core	3.46	0.4452	0.4481	0.08
CAS-SCF, 6*e* in 6 orb. DZ + D Basis	3.58	0.0726	0.0750	0.07

For Dewar benzene the 6-31G optimized geometry has been employed

[33], indicated in the first two rows of Table 4, this approach should be theoretically the best among the various variants of Table 4, and it gives a correlation energy difference between the two isomers of about 0.30 eV, only slightly larger than the value of the MP2 procedure in Table 3. It also shows that even though the transformation from benzene to its Dewar form is qualitatively

described by the HOMO and LUMO's in Fig. 2, the quantitative correlation treatment must include the σ orbitals also.

Prior experience [34] has shown, that the use of localized MO's (LMO) leads to faster CI convergence than delocalized orbitals, in particular if electron correlation can be considered as a fairly local effect, and so it is not surprising that the MCPF treatment correlating only 18 electrons (assuming the correlation energy in the benzene and Dewar benzene CH bonds to be equal) gives essentially the same isomerization energy as the more extended treatment which correlate 30 electrons.

The conclusion that can be drawn from the results in Table 3 is, that the correlation energy difference between the two isomers is in the order of 0.3 eV, and that the isomerization energy, measured as the energy difference between the two minima in the potential surface, lies around 3.35 eV.

If comparison is made with experiment, we notice two points. First, the Dewar geometry, optimized in the 6-31G AO basis employing the SCF treatment, varies considerably from that derived experimentally on the basis of electron diffraction experiments [28]. The parameters for the minimum energy structure are compared in Table 5. The largest discrepancies are seen in the the CH bond lengths, which are considerably longer in the experimentally derived structure, and in the angle of the central bridge-hydrogens, which differs by as much as 14° in the two geometry determinations. Note, that the estimated error from this geometrical parameter is 3° in the electron diffraction work, i.e., much larger than the error limits for the other geometrical variables.

This finding is not an artefact of the SCF treatment. MCPF calculations correlating 30 electrons (in the manner of the calculations of the first row of Table 3) confirm that a value of 121° for $<C_6C_3H_9$ is energetically preferred over one which is increased by +3° or decreased by 3° or even 6°. Semiempirical MNDO calculations carried out by us also find shorter C_3–H_9 (1.09 Å) and C_1–H_7 (1.07 Å) distances and a larger $<C_6C_3H_9$ angle (123.8°) than in Ref. [28], similar to the present *ab initio* treatment. Improvement of the AO basis set does not change the situation: the SCF treatment employing a 6-31G* basis instead of the 6-31G AO set predicts optimal bond lengths of 1.08 Å (C_3–H_9), 1.07 Å (C_1–H_7), and an angle of 121.8° ($<C_6C_3H_9$) instead of the 6-31G values of 1.078 Å, 1.07 Å, and 122.2° respectively.

Table 5. Optimized coordinates for Dewar benzene and comparison with experiment [28]

Parameters	Ref. [28]	6-31G opt.
C_3–C_6	1.574(0.005)	1.579
C_2–C_3	1.524(0.002)	1.534
C_1–C_4	1.345(0.001)	1.331
C_3–H_9	1.134(0.004)	1.078
C_1–H_7	1.124(0.004)	1.07
$<C_1C_6C_5$	116.7(0.6)	116.6
$<C_3C_6C_1$	85.7(0.2)	85.4
$<C_6C_3H_9$	108(3.0)	122.2
$<C_3C_2H_8$	126.7(2.5)	131.9
ϕ	117.25(0.6)	117.2

As a consequence of this different Dewar benzene geometry the SCF energy changes by as much as 0.68 eV if the structural parameters of Ref. [28] are employed instead of those of the 6-31G optimized geometry. Note, however, that the experimental geometry is only employed for the results of Fig. 3, which is intended to show only the qualitative behavior of the various states. The calculated energy difference between the optimized and the experimental Dewar benzene structure varies somewhat with the theoretical treatment; the difference is 0.64 eV in the MRD-CI treatment (DZ + D AO basis) and 0.45 in the MCPF approach (DZ + D). The optimization of all parameters for the aromatic benzene structure leads to parameters which differ only very slightly from the experimentally well-known bond lengths (CC = 1.388 Å and CH = 1.073 Å instead of the measured 1.395 Å and 1.088 Å). These deviations are of the same order as those for the CC bonds in Dewar benzene (Table 5). The energetic SCF difference between the aromatic benzene structure in the experimental and in the 6-31G optimized geometry is only 0.0011 a.u. or 0.03 eV, i.e., negligible compared to the 0.68 eV difference in the Dewar form. We feel therefore very strongly that a new experimental determination of geometrical parameters of the benzene Dewar form is required, in particular in light of the standard errors in electron diffraction structural determinations [35].

The second point concerns the substitution effect. One generally reads that the thermal rearrangement of Dewar benzenes to benzenes is about 60 kcal/mol [36–38] or 2.60 eV. As far as we know, this quantity has not been determined for the unsubstituted compound. Detailed measurements are available for hexamethylbenzene [36] and find $\Delta H^\circ = -56.2 \pm 0.6$ kcal/mol (2.44 eV) or 59.4 kcal/mol (2.58 eV) [39]. Our SCF calculations (Table 6) find an energy difference between the two hexamethylbenzene isomers of 3.05 eV, i.e., considerably lower than for benzene itself. In this instance the geometry of the aromatic and Dewar forms have been optimized on the MNDO level of treatment, and these geometries are employed in the ensuing 6-31G SCF calculations. We assume that the deviation from an SCF calculation which employs the geometrical parameters actually optimized in the 6-31G basis rather than by MNDO is only a few tenths of an eV, since MNDO and 6-31G-optimized geometries are generally very similar. Our MNDO optimized geometry for

Table 6. Influence of substitution on the isomerization energy of benzene – Dewar benzene

Treatment	E_{iso} (eV) benzene	E_{iso} (eV) hexamethyl-b.
SCF, 6-31G basis	4.35[a]	3.05[b]
MNDO	2.96	1.30
Experiment (ΔH°)		2.44[c], 2.58[d]

[a] 6.31G optimized geometry for Dewar benzene. The effect of the zero-point energy is to lower the energy difference by about 0.07 eV

[b] MNDO optimized geometry for both isomers

[c] Ref. [36]

[d] Ref. [39]

hexamethylbenzene is within the standard error limits (a few hundredths of an Å) of the DZ optimized geometry [40]; it shows a difference of 1.88 kcal/mol (MNDO-level) between the fully planar C_{6h} structure and the preferred slightly out-of-plane D_{3d} symmetry. The DZ calculations [40] have previously supported the nuclear diffraction data [41] rather than those obtained from electron diffraction [42]. If the MNDO calculations are considered than in the SCF treatment an even more dramatic change is seen in E_{iso} for benzene and hexamethylbenzene. As a result it seems obvious that substitution can lower the isomerization energy, and that isomerization energies, computed for benzene itself, cannot be directly compared with those for compounds with substituents.

On the basis of the results of Table 4 one expects that inclusion of correlation energy would lower E_{iso} for hexamethylbenzene by 0.3 eV to a theoretically obtained value of 2.75 eV. The use of a better AO basis than 6-31G is expected to lower the difference further (Table 3). Whether this basis set correction can be considered a constant, or whether it requires a scaling factor, is not clear. In any event, it will lead to a value considerably below 2.75 eV. For a comparison with ΔH° the difference in zero-point energies of the two isomers must furthermore be considered. If the ω values available for benzene [43] and Dewar benzene [44] in the literature are taken, the sum of zero-point energies of Dewar benzene is lower by 537 cm^{-1} or 0.07 eV. Given the various uncertainties in the geometry for both hexamethylbenzene isomers employed and deficiencies in the AO basis set, the discrepancy to the measured values around 2.5 eV is not alarming.

In conclusion we feel that the presently calculated value around 3.35 eV (Table 4) for the electronic energy difference of the two benzene isomers is realistic. It should furthermore be kept in mind that substituents can lower the isomerization energy substantially.

4. [*n*] Paracyclophanes, $n = 5, 6, 7$

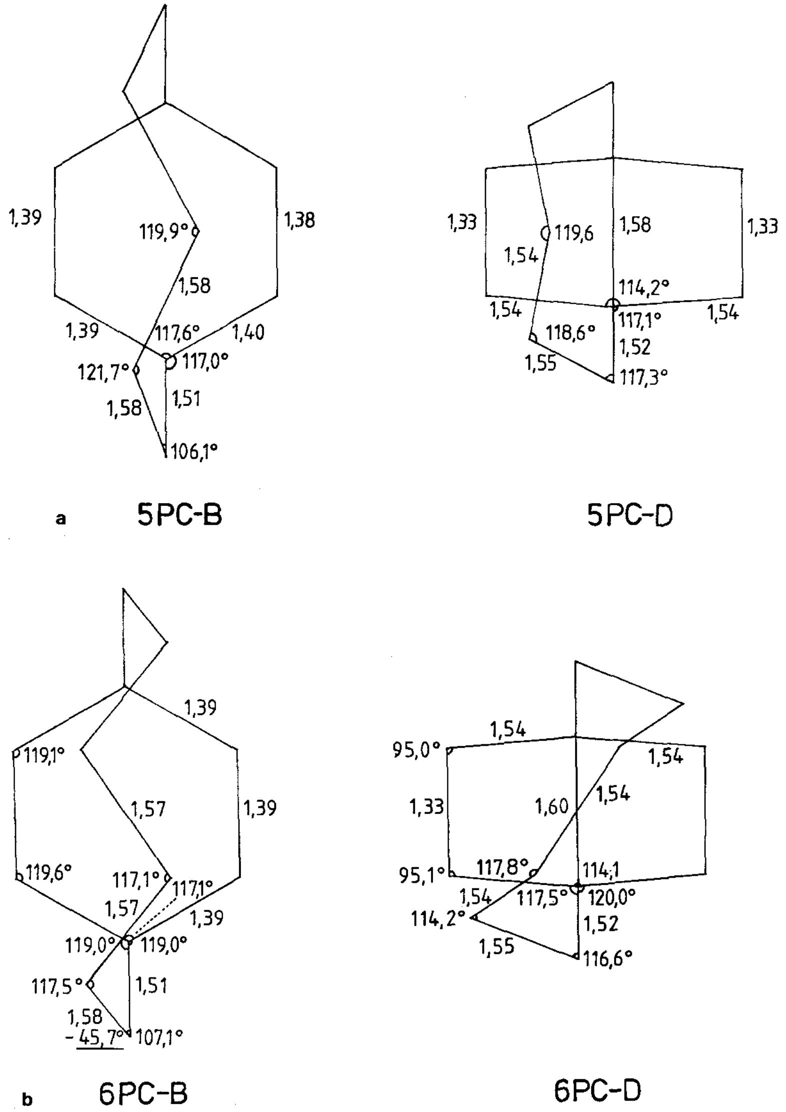
4.1. Geometry

The geometry optimization for the [*n*]paracyclophanes ($n = 5, 6, 7$) in their aromatic and Dewar type forms was undertaken at the SCF level employing the 6-31G AO basis. The values obtained are collected in Fig. 4. The most important data, i.e. the deformation angle α of the benzene ring, or alternatively the Dewar angle ϕ as well as the distance L between the two carbon atoms next to the $(CH_2)_n$ chain (Fig. 1) are collected in Table 7. From these data it is obvious that the Dewar skeleton is essentially unaffected by the $(CH_2)_n$ bridge, and that the shortening of the $(CH_2)_n$ bridge moves the benzene form on the "reaction coordinate" of Fig. 3 from its $\alpha = 0^\circ$ minimum towards the isomerization barrier.

Comparison with data from other authors is made in Table 8. All methods give the same systematic trend. The semiempirical AM1 data are always below those of the original MNDO procedure. The molecular mechanics (MM and force field FF) data obviously depend on the parameters used. Very few experimental values are available, and given the fact, that they are for substituted compounds generally in crystals, there is a convincing relationship to our presently calculated geometrical data.

4.2. Isomerization energies

For the [*n*]paracyclophanes SCF calculations are no more practical in the large AO basis sets, which are in principle required for determining stability differences. Similarly, computations accounting for electron correlation in the entire system are not feasible. Hence SCF calculations for the entire systems are only undertaken in the 6-31G AO basis, in which the geometry optimization has been carried out, and in addition in the DZP basis, which takes into account polarization effects and seems to be the smallest AO basis which can be employed to obtain meaningful energy differences (Table 3). The results given in Table 9 show a similar lowering (0.5 eV) in the energy difference from the 6-31G to DZP basis as has been found for benzene itself (Table 3).



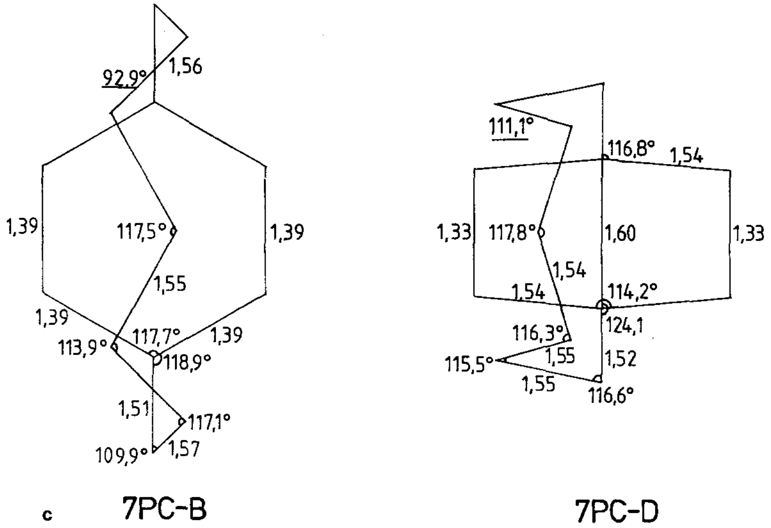


Fig. 4a–c. Geometries of the various [*n*]paracyclophanes and their Dewar isomers

Table 7. Comparison of calculated geometrical parameters characteristic for the deformation of the benzene ring in $n = 5$, 6, and 7 paracyclophanes

	α (°)	ϕ (°)	L (Å)
Benzene form			
$n = 5$ (C_s)	23.5	152.8	2.71
$n = 6$ (C_2)	18.8	158	2.75
$n = 7$ (C_s)	14.1	163	2.78
$n = \infty$ (benzene)	0.0	180	2.79
Dewar form			
$n = 5$ (C_s)	81.3	114.8	1.58
$n = 6$ (C_2)	80.7	114.8	1.60
$n = 7$ (C_s)	80.8	114.9	1.60
$n = \infty$ (D-benzene)	81.1	117.2	1.58

In order to account for the correlation energy error between the two isomers the easiest would be to simply substract the benzene correlation energy difference ΔE_{corr} (approximately 0.3 eV, Table 4) from the DZP values for the various [*n*]paracyclophanes in Table 9. On the other hand, this difference (at least for the benzene skeleton) is not expected to be the same for the various *n*. It should be of the same order as in benzene for $n = 7$, in which the Dewar form is very similar to Dewar benzene and the phane is only slightly deformed from the benzene ring; it should be smaller for $n = 5$ because in this compound the phane and Dewar type structures are more similar.

An obvious calculational procedure to support this idea quantitatively is the following: the $(CH_2)_n$ bridge is formally removed and replaced by two hydro-

Table 8. Deformation angle α of the benzene skeleton in various [*n*]paracyclophanes obtained from different methods

	SCF, 6-31G present	SCF, double-ξ Ref. [5, 6]	MNDO Ref. [18]	AM1 Ref. [12]	FF Ref. [19]	MM Ref. [20]	Expt.
$n = 5$	23.5	23.7	31.4	28.6	26.6	35.9	—
$n = 6$	18.8	18.6	25.3	22.8	22.4	22.8	—
$R_1 = COOH$				23.2			20.5[a]
$R_1 = R_2 = COOCH_3$							19.5[b]
$n = 7$	14.1	14.2	19.9	17.1	18.2	15.0	—
$R_1 = COOH$							18.3/15.2[c]

[a] Ref. [49]
[b] Ref. [9]
[c] Ref. [50]

Table 9. SCF results (in eV) for the energy differences between the benzene and Dewar benzene-type structures of [*n*]paracyclophanes (geometries optimized at the 6-31G level). The last row contains the results if only the benzene skeleton without the $(CH_2)_n$ bridge is considered

Basis	$n = 5$	$n = 6$	$n = 7$
6-31G	1.41	2.52	3.57
DZP	0.91	1.98	3.03
DZP (C_6H_6 skeleton)	1.30	2.35	3.06

gens, but the C_6H_6 skeleton is maintained as in the [*n*]paracyclophane geometry. The results are also contained in Table 9. The difference in the SCF isomerization energies of the entire molecule and the C_6H_6 skeleton is due to the $(CH_2)_n$ chain, and can be considered as loss of internal strain energy of the $(CH_2)_n$-bridge during the deformation from the benzene to the Dewar benzene type isomer. The benzene skeleton can then be treated by the same procedures as benzene itself (Table 10).

The first two calculations should be the most reliable, as discussed in connection with the benzene isomerization. The qualitative arguments on correlation energy contribution are confirmed. The isomerization energy decreases substantially from benzene to [5]paracyclophane.

5. Summary and conclusion

The relative energetics of the various [*n*]paracyclophanes as deduced from the present study are indicated in Fig. 5. The same "reaction coordinate" as in Figs. 2 and 3 is assumed. The geometry of all the Dewar structures is very similar and therefore the minima of these structures are chosen as the zero of energy in the figure. The potential wells of the aromatic structures lie formally on the pathway

Table 10. Isomerization energies for [*n*]paracyclophanes (in eV) obtained by treating the C_6H_6 skeleton in the respective cyclophane geometry and accounting for the contribution of the chain (i.e. 0.39 eV for $n = 5$, 0.37 eV for $n = 6$ and 0.03 eV for $n = 7$, according to Table 9, SCF, DZP value)

	$n = 5$	$n = 6$	$n = 7$
MCPF, 30*e*, DZ + D canon. MO, 1*s* in core	0.78	1.64	2.58
MCPF, 18*e*, DZ + D LMO, 1*s* plus CH in core	0.70	1.63	2.60
MRD-CI, 20*e*, DZ + D canon, MO, MO with $\epsilon < -0.8$ in core	0.77	1.71	2.68
CAS-SCF, DZ + D 6*e* in 6 orbitals	0.93	1.87	2.82

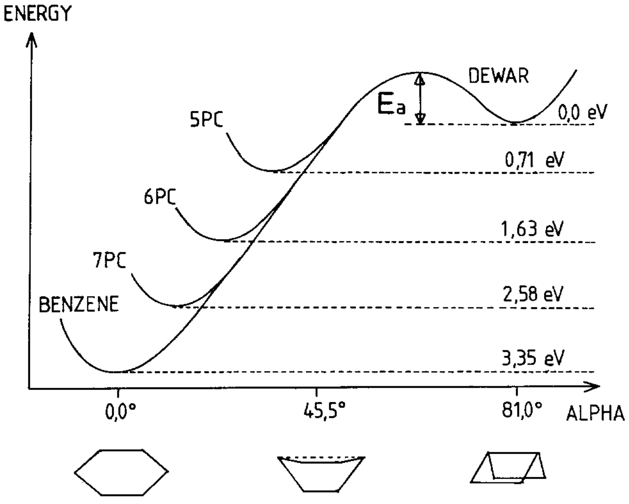


Fig. 5. Schematic picture of the relative energetics of [*n*]paracyclophanes and their Dewar isomers, including the parent molecules benzene and Dewar benzene. The relative energies result from *ab initio* calculations employing a double zeta plus polarization AO basis plus inclusion of electron correlation effects

from benzene to Dewar benzene and hence the energy difference between the isomers decreases fast with decreasing *n*. The potential barrier E_a is primarily determined by the crossing of two orbitals and, as indicated in Fig. 5, is expected to be of similar height for all Dewar benzene type [*n*]paracyclophanes. This has been discussed on the basis of experiments, for various substitutes R_1 and R_2 in [6]paracyclophane and similar systems in Ref. [10, 11]. On the basis of the potential energy curves (Fig. 3) the trend in the location of the low-lying excited states in the various [*n*]paracyclophanes can also be extracted.

An analogous situation has been found in the photochemical valence isomerization of 9-alkylsubstituted anthracene to its 9-10 Dewar isomer [45, 46]. From the spectroscopic, caloric and kinetic data an energy diagram for the process has been constructed [46], in which the folding along the 9, 10 axis of the anthracene skeleton served as the main reaction coordinate. This coordinate is equivalent to the benzene ring deformation angle ϕ shown in Fig. 1. Steric interaction of bulky substituents, such as t-butyl groups, causes already a folding of about 13° of the anthracene frame [46], which is equivalent to a $\phi = 167°$ deformation of the benzene ring (i.e. about that found for [7]paracyclophane, Table 7). Just as discussed in the present work, the energy difference between the Dewar isomer and the anthracene isomer is reduced by this deviation from the planar ring structure.

The calculated energies for the relative stability of the unsubstituted [*n*]paracyclophanes and their Dewar isomers as obtained from the best treatment are also indicated in Fig. 5. There is a possibility that substituents lower the Dewar side of the potential. Such behavior would be supported by the calculation of the isomerization energy of hexamethylbenzene. As a consequence, the activation energy for the reverse reaction E_a, is expected to increase. An alternate possibility is, that substituents facilitate the benzene ring deformation even more, so that the minima of the [*n*]phanes are shifted further to the right in Fig. 5 (decreasing the isomerization energies). Both alternatives would be consistent with the observed low value of $\Delta H = -19.8 \pm 3$ kJ/mol for the thermal back reaction of the $n = 6$ compound [10] even though the present value for the unsubstituted system is considerably larger.

The present calculations have shown that AO basis sets of at least double-zeta quality including polarization functions are necessary for an adequate description of the relative energetics; correlation effects are also found to be not negligible. They discuss the trends of the various [*n*]paracyclophanes, in their geometrical and energetic behavior in terms of a single potential surface diagram. It would be interesting to study in more detail the area of the potential barrier in the photoreaction, together with the electronically excited states on one hand, and details of the substituent effects on the stability behavior on the other.

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