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[4]PARACYCLOPHANE: MNDO AND STO-3G MOLECULAR STRUCTURE AND STRAIN ENERGY*

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The molecular structure of [4]paracyclophane was optimized at the semiempirical MNDO and the *ab initio* STO-3G level. A comparison of the results showed that the benzene ring is much less bent at the STO-3G level. Although some bond alternation is predicted at both levels of theory, the aromatic carbon—carbon bond lengths are still in the range typical of highly delocalized compounds. The calculated strain energy [*SE*(tot.)] of [4]paracyclophane is larger for the STO-3G structure. Nevertheless, the distributions of *SE*(tot.) over the bent benzene ring [*SE*(bb.)] and the oligomethylene bridge [*SE*(br.)] are the same for the MNDO and STO-3G structures.

INTRODUCTION

The synthesis of [*n*]paracyclophanes with $n < 7$ has presented a particular challenge to experimental chemistry.[2,3] [6]Paracyclophane is isolable and stable at ambient temperature.[4–6] X-ray structure determinations of crystalline derivatives[7–9] have confirmed the theoretically predicted boat shape of the bent benzene ring.[10–15] [5]Paracyclophane, in contrast, is not isolable and only stable in solution below 273 K.[16] It has been characterized by ^{1}H NMR and UV spectroscopy. Recently, the intermediacy of the next lower homologue, [4]paracyclophane, was invoked on the basis of trapping experiments.[17,18] [4]Paracyclophane itself has only been identified tentatively by its UV spectrum at 77 K.[18] In line with intuition, the characterization of [4]paracyclophane is thwarted by the increase in strain with decreasing n in the series $n = 6$, 5 and 4. This is supported by theoretical calculations at different levels of theory for [6]- and [5]paracyclophane.[10–15,19] We are not aware of any previous theoretical investigation of the elusive [4]paracyclophane. We report here the results of semiempirical MNDO[20] and *ab initio* calculations with the STO-3G basis set[21] for [4]paracyclophane.

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COMPUTATIONAL PROCEDURES

All calculations on [4]paracyclophane were executed at the self-consistent-field (SCF) level of theory. MNDO[20] as implemented in MOPAC[22] was used for the semiempirical calculations. The molecular structure of [4]paracyclophane was optimized without any geometric constraints. For the *ab initio* calculations the STO-3G minimal basis set[21] as implemented in GAUSSIAN 80[23] was used with the optimized MNDO structure of [4]paracyclophane as input geometry. Again, no geometric constraints were imposed during the optimization; all gradients were smaller than 1×10^{-4} hartree bohr^{-1}. Note that STO-3G performed well with [5]-, [6]-, [7]- and [8]paracyclophane[14,15,19] and with hydrocarbons in general.[24] Since for the higher homologues both MNDO[11] and STO-3G[14,15,19] data are available, we would expect a theoretical investigation of [4]paracyclophane at similar levels of theory to be of interest for comparison within the series.

RESULTS AND DISCUSSION

Molecular structure of [4]paracyclophane

With both MNDO and STO-3G a genuine minimum could be located for [4]paracyclophane; all force constants were positive.[25] Pertinent results of the calculated geometries are shown in Tables 1 and 2. The projected angles α, β and γ and the numbering of the carbon atoms are defined in Figures 1 and 2. [4]Paracyclophane is predicted to possess C_2 symmetry

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Table 1. Calculated projected angles α, β and γ of [4]paracyclophane[a]

Angle(°)	MNDO	STO-3G
α_1, α_2 ($\alpha_{av.}$)[b]	39·0, 38·3 (38·7)	29·3, 27·3 (28·3)
β	29·3	39·5
γ	7·8	10·9

[a] For a definition of α, β and γ, see Figure 1.
[b] See text; $\alpha_1 = \tau$(C-6, C-7, C-9, C-8), $\alpha_2 = \tau$(C-10, C-9, C-7, C-8) and $\alpha_{av.} = (\alpha_1 + \alpha_2)/2$.

both at the MNDO and STO-3G levels of theory. This is in agreement with experimental[2,7-9] and theoretical[10-15] data obtained for higher homologues in the [*n*]paracyclophane series with *n* even. Owing to the C_2 symmetry, the projected angle α, which indicates the bending of the 'bow' of the boat from the original benzene plane and thus is a measure of the deviation from planarity of the bent benzene ring, is not unambiguously defined; formally, C-6, C-7, C-9 and C-10 do not have to lie in the same plane. However, in both the MNDO and STO-3G molecular structures of [4]paracyclophane the deviation is very small; the torsional angles $\alpha_1 = \tau$(C-6, C-7, C-9, C-8) and $\alpha_2 = \tau$(C-10, C-9, C-7, C-8) take values of 39·0° and 38·3° in the MNDO and 29·3° and 27·3° in the STO-3G molecular structures of [4]paracyclophane (Figures 1 and 2 and Table 1). For comparison we have also included the average values of α($\alpha_{av.}$) in Table 1. A survey of the calculated values of α reveals that the benzene ring of [4]paracyclophane is much less bent in the STO-3G structure. In contrast, the projected angle β, which has only a single value in [4]paracyclophane, is calculated to be considerably larger at the STO-3G level [Figure 1 and Table 1: $\beta = 39{\cdot}5°$ (STO-3G) and 29·3° (MNDO)]. Since for [6]paracyclophane STO-3G, in contrast to MNDO, predicted values of α and β that were close to those found in the x-ray structure determinations of crystalline derivatives, we anticipate that for [4]paracyclophane also the STO-3G results will be more reliable.[14,15]

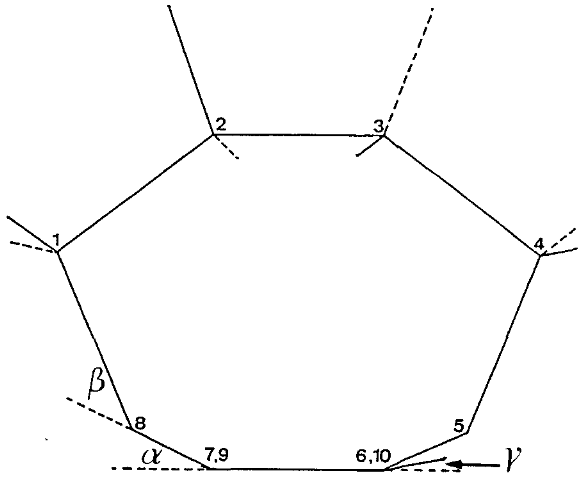

Figure 1. Theoretical molecular structure of [4]paracyclophane based on the STO-3G calculation; side view (projected on a plane perpendicular to C-7—C-9)

In agreement with the available experimental[2,7-9] and theoretical[10-15] evidence for higher homologues, all substituents of the benzene ring are predicted to deflect towards the concave side; they are all located on the same side as the oligomethylene bridge (Figure 1 and Table 1; α, β and γ). Apparently, the observed direction

Table 2. Selected structural parameters of [4]paracyclophane and *p*-xylene[a]

	[4] Paracyclophane		*p*-Xylene	
Parameter	MNDO	STO-3G	MNDO	STO-3G
Bond lengths (Å):				
C-5—C-6	1·434	1·404	1·411	1·391
C-6—C-7	1·400	1·377	1·405	1·385
C-7—C-8	1·431	1·403	1·411	1·390
C-1—C-8	1·500	1·530	1·506	1·527
C-1—C-2	1·585	1·603	—	—
C-2—C-3	1·547	1·592	—	—
Valence angles (°):				
C-6—C-5—C-10	116·4	116·6	118·0	118·2
C-5—C-6—C-7	114·7	117·1	121·0	121·0
C-6—C-7—C-8	113·5	118·0	121·0	121·0
C-8—C-1—C-2	107·4	105·9	—	—
C-1—C-2—C-3	125·7	123·3	—	—

[a] For numbering, see Figure 2. For convenience, the same numbering is used for *p*-xylene.

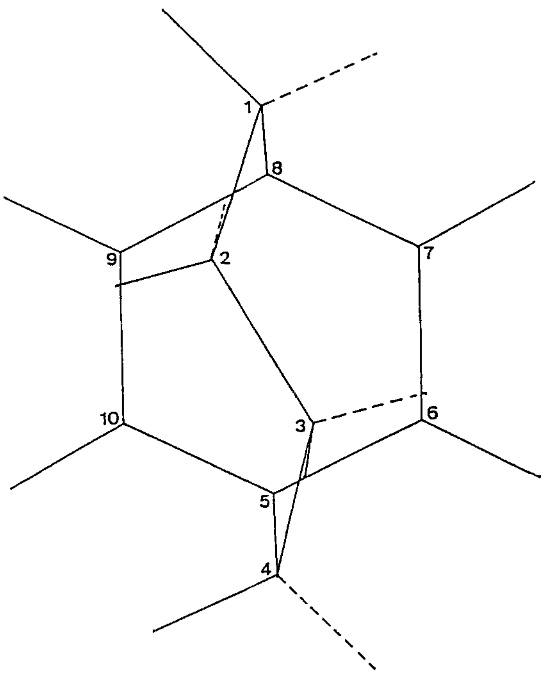

Figure 2. Theoretical molecular structure of [4]paracyclophane based on the STO-3G calculation; top view (projected on the plane defined by C-6, C-7 and C-9)

of deflection is a consequence of the optimization of p-orbital alignment in the bent benzene ring, which can be accomplished by rehybridization.[26] This is corroborated by an inspection of the sum of valence angles [Figure 2: sum of valence angles STO-3G (MNDO); C-5 $\Sigma = 344{\cdot}5^\circ$ ($351{\cdot}9^\circ$), C-6 $\Sigma = 355{\cdot}3^\circ$ ($358{\cdot}8^\circ$) and C-10 $\Sigma = 356{\cdot}3^\circ$ ($358{\cdot}9^\circ$)]. Especially for the bridge-head carbon atoms C-5 and C-8 substantial rehybridization (pyrimidalization) is found. Note that it is more pronounced in the *ab initio* than in the semiempirical structure of [4]paracyclophane.

The calculated carbon—carbon bond lengths of the bent benzene ring of [4]paracyclophane vary in the range 1·400–1·434 Å (MNDO) and 1·378–1·404 Å (STO-3G, Figure 2 and Table 2). In comparison, values of 1·405–1·411 Å and 1·385–1·391 Å, respectively, are calculated for the unstrained reference compound *p*-xylene (Table 2).

Intriguingly, the variation in the aromatic carbon—carbon bond lengths of [4]paracyclophane at the STO-3G level is smaller than that of [5]paracyclophane (STO-3G: 1·365–1·412 Å).[19] Moreover, a different tendency towards localization in the bent benzene ring of both compounds is predicted by STO-3G. For [5]paracyclophane some bond fixation is calculated towards a cyclohexa-1,3,5-triene-like structure[19], whereas for [4]paracyclophane a trend is observed towards a Dewar benzene-like structure (cf. Table 2). A comparison of the available STO-3G structural data for the bent benzene rings in [8]-, [7]-, [6]-, [5]- and [4]paracyclophane suggests that the observed sequence of bond length alternation in the STO-3G molecular structures of the highly strained representatives ($n < 7$) is related to the symmetry of the [*n*]paracyclophane, i.e. C_2 symmetry (*n* is even) imposes a Dewar benzene-type geometry, where C_s symmetry (*n* is odd) favours a more cyclohexa-1,3,5-triene-type geometry (Table 3). From [6]- to [4]paracyclophane an increasing distortion of the bent

Table 3. STO-3G and MNDO calculated aromatic carbon—carbon bond lengths (Å) of [8]-, [7]-, [6]-, [5]- and [4]paracyclophane[a]

		[*n*]- and symmetry				
	Method	[8]-, C_2	[7]-, C_s	[6]-, C_2	[5]-, C_s	[4]-, C_2
C-5—C-6	STO-3G	1·391	1·390	1·394	1·382	1·404
	MNDO	1·415	1·418	1·421	1·423	1·434
C-6—C-7	STO-3G	1·384	1·382	1·382	1·396	1·377
	MNDO	1·403	1·401	1·401	1·403	1·400
C-7—C-8	STO-3G	1·391	1·390	1·393	1·382	1·403
	MNDO	1·417	1·418	1·421	1·423	1·431
C-8—C-9	STO-3G	1·391	1·393	1·394	1·412	1·404
	MNDO	1·415	1·418	1·421	1·428	1·434
C-9—C-10	STO-3G	1·384	1·384	1·382	1·365	1·377
	MNDO	1·403	1·401	1·401	1·398	1·400
C-5—C-10	STO-3G	1·391	1·393	1·393	1·412	1·403
	MNDO	1·417	1·418	1·421	1·428	1·431
Ref.		15, 27	11, 15	11, 14	11, 19	This work

[a] For convenience the numbering shown in Figure 2 is used.

benzene ring is found. As expected, the less strained [7]- and [8] paracyclophane possess aromatic carbon—carbon bond lengths in the range expected for ordinary 1,4-dialkylbenzene derivatives (cf. Tables 2 and 3). However, we feel that one should be careful in interpreting these differences. Note that the symmetry dependence of the sequence of bond length alternation is hardly discernible at the MNDO level of theory for the highly strained representatives ($n < 7$). In all cases, a Dewar benzene-like distortion is calculated (Table 3). Further, it has been shown that for [5] paracyclophane the bond length alternation decreases at higher levels of theory (DZ-SCF: 1·384–1·409 Å).[19] Nevertheless, the calculated aromatic carbon—carbon bond lengths for [4] paracyclophane still fall in the range for highly delocalized compounds.[28] The valence angles of the bent benzene ring are found to deviate less in the STO-3G structure than in the MNDO structure from the reference values obtained for *p*-xylene (Table 2). Apparently, the oligomethylene bridge exerts a larger compression effect on the benzene ring at the MNDO level of theory. This is supported by the calculated structural parameters of the oligomethylene bridge.

As expected, the less rigid sp^3-hybridized carbon atoms of the bridge are more capable of responding to strain by variation in bond length and valence angle from their reference values (bond lengths: C_{sp^2}—C_{sp^2} 1·50 Å, C_{sp^3}—C_{sp^3} 1·54 Å and valence angle 109·5°).[29] A survey of the calculated bond lengths for the bridge shows that, especially in the STO-3G structure, large deviations are predicted (Figure 2 and Table 2). For example, the carbon—carbon bond lengths C-1—C-2 (1·603 Å), C-2—C-3 (1·592 Å) and C⁻—C′ (1·530 Å) of the STO-3G structure are considerably longer than in the MNDO structure (1·585, 1·547 and 1·500 Å, respectively). On the other hand, the valence angles C-8—C-1—C-2 and C-1—C-2—C-3 have nearly the same value in both structures. Consequently, the oligomethylene bridge appears to be a more rigid clamp by the MNDO calculations; the benzene ring responds with more pronounced deviations at the MNDO level of theory (see above).

Strain energy of [4] paracyclophane

An estimate of the strain energy [*SE*(tot.)] of [4] paracyclophane can be obtained by applying the following homodesmotic reaction for which $SE(\text{tot.}) = -\Delta E$:[30]

$$[4]\text{paracyclophane} + 5C_2H_6 \rightarrow p\text{-xylene} + 4C_3H_7$$

From the results presented in Table 4, *SE*(tot.) = 88·5 and 125·95 kcal mol⁻¹ are calculated at the MNDO and STO-3G levels, respectively, for [4] paracyclophane. To gain an insight into the distribution of *SE*(tot.) over the bent benzene ring [*SE*(bb.)] and the oligomethylene bridge [*SE*(br.)], which are related by

$$SE(\text{tot.}) = SE(\text{bb.}) + SE(\text{br.})$$

we performed a single-point calculation on benzene frozen in the conformation present in [4] paracyclophane. The additional hydrogen atoms were placed at a typical aromatic carbon hydrogen distance (STO-3G 1·083 Å, MNDO 1·086 Å) in the same direction as C-1 and C-4, respectively, of the bridge. Values of *SE*(bb.) = 77·0 and 111·83 kcal mol⁻¹ were calculated with MNDO and STO-3G, respectively.

A referee suggested that *p*-xylene frozen in the conformation present in [4] paracyclophane would be a better reference compound for the evaluation of *SE*(bb.), since part of the bond length changes in the aromatic moiety are a consequence of alkyl substitution already present in the equilibrium structure of *p*-xylene compared with benzene. However, with MNDO a value of *SE*(bb.) = 78·6 kcal mol⁻¹ is calculated with *p*-xylene as the reference compound, which is nearly the same as the *SE*(bb.) = 77·0 kcal mol⁻¹ obtained with benzene {cf. Ref. 31 for a similar analysis of *SE*(bb.) in

Table 4. MNDO heats of formation (ΔH_f°), STO-3G total energies (E) and strain energies (SE) of [4] paracyclophane and related compounds

Compound	STO-3G: E (hartree)[a]	MNDO ΔH_f° (kcal mol⁻¹)	*SE*(tot.)(kcal mol⁻¹)		*SE*(bb.)(kcal mol⁻¹)		*SE*(br.)(kcal mol⁻¹)	
			STO-3G	MNDO	STO-3G	MNDO	STO-3G	MNDO
[4] Paracyclophane	−380·874025	93·0	125·95	88·5	111·83	77·0	14·12	11·5
p-Xylene	−305·059912	5·6	—	—	—	—	—	—
Bent benzene[b]	−227·713171	98·2	111·83	77·0	111·83	77·0	—	—
Benzene	−227·891361[c]	21·2[d]	—	—	—	—	—	—
Propane	−116·886422[c]	−24·9[d]	—	—	—	—	—	—
Ethane	− 78·306180[c]	−19·7[d]	—	—	—	—	—	—

[a] 1 hartree = 627·50 kcal mol⁻¹.
[b] See text.
[c] Taken from Ref. 19.
[d] Taken from Ref. 20.

[n]metacyclophanes}.[1] Moreover, bent benzenes are commonly used for the determination of *SE*(bb.) in [n]cyclophanes.[14,15,19] The STO-3G values of *SE*(tot.), *SE*(bb.) and *SE*(br.) for [4]paracyclophane are consistently larger than the corresponding MNDO values (Table 4). Similar results were found with [5]- and [6]paracyclophane. For [5]- and [6]paracyclophane, values of *SE*(tot.) of 63·2 kcal mol^{-1} (MNDO) and 85·93 kcal mol^{-2} (STO-3G) and 54·0 kcal mol^{-1} (MNDO) and 56·62 kcal mol^{-1} (STO-3G), respectively, were calculated according to the abovementioned procedure.[14,19] Nevertheless, the ratios *SE*(bb.):(*SE*(tot.) and *SE*(br.):*SE*(tot.) for [4]paracyclophane are almost the same at both levels of theory [*SE*(bb.):*SE*(tot.) = 0·89 (STO-3G) and 0·87 (MNDO)]. This indicates that, despite the difference in absolute values, the distribution of *SE*(tot.) is similar in the MNDO and STO-3G structures of [4]paracyclophane.

As expected, the major proportion of *SE*(tot.) is due to the non-planarity of the benzene ring. Intriguingly, *SE*(bb.) far exceeds the resonance energy of benzene (20–30 kcal mol^{-1}).[28,29] Although this is sometimes taken as evidence for rejecting the aromatic character of [4]paracyclophane, our calculations indicate that the aromatic carbon—carbon bond lengths still fall in the range of highly delocalized compounds.[28] As discussed in the preceding section, substantial rehybridization of the aromatic carbon atoms of the bent benzene ring is calculated; this facilitates favourable p-orbital interactions despite the severe bending.[26] Until recently, the extraordinary chemical reactivity of small [n]cyclophanes was rationalized by invoking bond fixation of the bent benzene ring towards a cyclohexa-1,3,5-triene-like structure.[1-3] However, an MNDO calculation on [4]paracyclophane, in which the bent benzene ring is artificially distorted to a localized cyclohexa-1,3,5-triene (with C_{sp^2}—C_{sp^2} = 1·483 Å and C_{sp^2} = C_{sp^2} = 1·337 Å[32]) shows that its heat of formation (ΔH_f^o) is calculated to be 10·6 kcal mol^{-1} less then that of [4]paracyclophane proper. It is remarkable that the same difference in stability of 10 ± 1 kcal mol^{-1} was found for [4]- and [5]metacyclophane and for benzene itself.[31,32] In other words, even extreme bending of the benzene ring does not increase its tendency to localize towards a Kekulé-type structure.

CONCLUSIONS

The molecular structure of [4]paracyclophane was calculated at the semiempirical MNDO and *ab initio* STO-3G levels of theory; genuine minima were located. The bent benzene ring deviates less from planarity in the STO-3G then MNDO structure (Table 1). Despite its severe bending and the occurrence of some bond length alternation, the aromatic carbon—carbon bond lengths still fall in the range for highly delocalized compounds. Although the total strain energy [*SE*(tot.)] of [4]paracyclophane is larger at the STO-3G than MNDO level of theory, the distribution of *SE*(tot.) over the bent benzene ring [*SE*(bb.)] and the oligomethylene bridge [*SE*(br.)] is nearly the same; *SE*(bb.) comprises the largest part (nearly 90%) of *SE*(tot.). The predicted increase in *SE*(tot.) on going from [5]- to [4]paracyclophane parallels the difficulties encountered in the synthesis of the latter {Δ*SE*(tot.) = *SE*(tot., [4]paracyclophane) − *SE*(tot., [5]paracyclophane); STO-3G 40·02 kcal mol^{-1}, MNDO 25·3 kcal mol^{-1}}.[17-19]

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