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[4]METACYCLOPHANE: STO-3G MOLECULAR STRUCTURE, STRAIN ENERGY AND CNDO/S–CI ELECTRONIC TRANSITION ENERGIES

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The molecular structure of [4]metacyclophane is optimized at the *ab initio* STO-3G SCF level and a genuine minimum is located. In the STO-3G structure the benzene ring is less bent and geometrically distorted than in the previously reported MNDO structure. Although some bond alternation is calculated for the carbon–carbon bond lengths of the bent benzene ring, their values still fall in the range of highly delocalized compounds. Despite the fact that the STO-3G strain energy [SE(tot.)] is larger than the corresponding MNDO strain energy, the distribution of SE(tot.) over the bent benzene ring [SE(bb.)] and the oligomethylene bridge [SE(br.)] is similar. To facilitate the hitherto unsuccesful identification of [4]metacyclophane, its electronic transition energies were calculated with CNDO/S–CI using the STO-3G geometry as input geometry. The reliability of the CNDO/S–CI results was assessed by a comparison of calculated and experimental electronic transition energies for *p*- and, *m*-xylene, [5]para- and [5]metacyclophane and [4]paracyclophane following the same approach.

INTRODUCTION

Small [*n*]cyclophanes are of interest for the investigation of the occurrence of electron delocalization in bent benzenes. Consequently, their synthesis and characterization have received considerable attention in recent years.[1–3] In the [*n*]paracyclophane series both [5]-[4] and [4]paracyclophane[5,6] have been identified spectroscopically and characterised in solution and matrix, respectively. In contrast, in the [*n*]metacyclophane series, [5]metacyclophane is still the smallest unequivocally characterized representative.[7] Although semi-empirical MNDO[8] calculations indicated that the next lower homologue [4]metacyclophane is less strained than [4]paracyclophane[9,10] it has hitherto escaped spectroscopic identification. Nevertheless, compelling evidence for its formation as a fleeting intermediate was deduced from the thermolysis of its Dewar benzene valence isomer tricyclo[6.1.1.0(3,9)]deca-2,8(10)-diene in either sealed ampoules at 150–200 °C or by flash vacuum thermolysis at 400–500 °C.[12] Obviously, the severe thermolysis conditions used for its generation hamper the isolation and identification of the elusive [4]metacyclophane. Similar observations have been reported previously in attempted syntheses of [5]-[13] and [4]paracyclophane[14] by thermal isomerization of the corresponding 1,4-bridged Dewar benzene isomers. The available experimental data suggest that the identification of [4]metacyclophane will have to wait for new synthetic approaches. Note that also irradiation at −50 °C of tricyclo[6.1.1.0(3,9)]deca-2,8(10)-diene gave the cyclopropane edge-bridged prismane derivative which rearranged to a fulvene; no evidence for the formation of [4]metacyclophane was found.[15]

With respect to the theoretical investigation of small [*n*]cyclophanes, it has recently been shown that the minimal *ab initio* STO-3G[16] basis set gives an improved description of the geometries of these strained molecules in comparison with semi-empirical MNDO[9,17] and molecular mechanics[18–20] results; especially the extent of distortion of the benzene ring is better described. Although STO-3G results have been published for [*n*]paracyclophanes with $n = 8$, 7, 6, 5 and 4[10,22–24] and for [5]metacyclophane,[25] to our knowledge no data are available for [4]metacyclophane. In this paper we report its STO-3G molecular structure, strain energy [SE(tot.)] and the distribution of SE(tot.)

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over the bent benzene ring [SE(bb.)] and the oligomethylene bridge [SE(br.)]. To facilitate the experimental identification of [4]metacyclophane, which is expected to rely on low-temperature (matrix) UV–visible spectroscopy, its electronic transition energies were calculated with CNDO/S–CI[26] using the optimized STO-3G structure. The reliability of the CNDO/S–CI results was assessed by a comparison of calculated electronic transitions with available experimental data for *p*- and *m*-xylene and [5]para-, [5]meta- and [4]paracyclophane following the same approach.

COMPUTATIONAL PROCEDURES

The *ab initio* STO-3G[16] minimal basis set as implemented in Gaussian 80[27] was used: the MNDO structure of [4]metacyclophane was taken as input geometry. No geometrical constraints were imposed during the geometry optimization and all final gradients were smaller than 1×10^{-4} hartree bohr^{-1}. The electronic transitions of *p*- and *m*-xylene and [5] para-, [4]para-, [5]meta- and [4]metacyclophane were calculated with CNDO/S–CI[26] using optimised STO-3G structures as input geometries. For the CNDO/S–CI calculations a limited configuration interaction (4×4 CI) was used taking into account single excited configurations between HOMO − 1, HOMO, LUMO and LOMO + 1.

RESULTS AND DISCUSSION

STO-3G molecular structure of [4]metacyclophane

With STO-3G a genuine minimum was located for [4]metacyclophane; all force constants were positive.[28] Pertinent results of the calculated STO-3G geometry in combination with previously reported MNDO results[9] are presented in the Tables 1 and 2. A survey of the data reveals that, in spite of the qualitative agreement, considerable quantitative differences are found between the optimized MNDO and STO-3G structures. In contrast to [5]metacyclophane, which possesses C_s symmetry,[9,25] [4]metacyclophane is calculated to lack any molecular symmetry at both levels of theory. Consequently, the projected angles α, β, γ, δ, ε and ζ in [4]metacyclophane are defined ambiguously since the carbon atoms C-5, C-6, C-8 and C-9 of the bent benzene ring do not have to lie in the same plane (cf. Figure 1 and Table 1, projected angles with subscripts 1 and 2). However, as shown by the data, the differences between the related projected angles is modest. For comparison, average values of the projected angles of [4]metacyclophane are included in Table 1.

As expected, the values of all projected angles increase on going from [5]- to [4]metacyclophane at the STO-3G and MNDO level of theory. The sum of α and γ, which indicates the total bending of the boat from the original benzene plane and is a measure of the deviation from planarity of the bent benzene ring, shows that [4]metacyclophane is less bent in the STO-3G structure ($\alpha_{av.} + \gamma_{av.}$, STO-3G 45.2° and MNDO 51.6°). A similar observation was made for [5]metacyclophane ($\alpha + \gamma$, STO-3G 33.3° MNDO 41.7°).[9,25] In agreement with available experimental[29] and theoretical[9,25] results for [5]metacyclophanes, all substituents present on the bent benzene ring of [4]metacyclophane are predicted to deflect to the convex side; they are all located on the same side as the oligomethylene bridge (Figure 1). An inspection of the sum of valence angles (Σ) of the carbon atoms of the bent benzene ring indicates that substantial rehybridization (pyrimidalization) occurs for the bridgehead carbon atoms C-5 and C-9, and the carbon atom C-10 at the 'bow' of the molecule [Figure 2 and Table 2; sum of valence angles Σ, STO-3G (MNDO), C-5 351·3° (354·7°), C-6 359·7° (359·7°), C-7 358·2° (359·7°), C-8 359·5°(359·6°), C-9 348·6° (354·2°) and C-10 350·7° (356·4). It should be noted that for

Table 1. STO-3G and MNDO calculated projected angles of [5]- and [4]metacyclophane[a]

	STO-3G		MNDO	
Angle (°)	[4]	[5][25]	[4][c]	[5][9]
α_{av}[b]	30·7 (α_1 30·3, $\alpha_2$31·0)	22·2	41·2 (α_1 40·6, α_2 41·7)	32·5
β_{av}[b]	48·5 (β_1 49·2, $\beta_2$47·7)	40·9	46·0 (β_1 46·1, β_2 45·8)	43·1
γ_{av}[b]	14·5 (γ_1 15·4, $\gamma_2$13·6)	11·1	10·4 (γ_1 12·0, γ_2 8·8)	9·2
δ_{av}[b]	24·8 (δ_1 26·4, $\delta_2$23·1)	17·9	21·0 (δ_1 23·4, δ_2 18·6)	7·7
ε_{av}[b]	13·3 (ε_1 13·6, $\varepsilon_2$12·6)	9·4	5·5 (ε_1 6·5, ε_2 4·5)	4·6
ζ_{av}[b]	30·1 (ζ_1 30·1, $\zeta_2$30·1)	19·5	17·2 (ζ_1 17·2, ζ_2 17·2)	13·9

[a] For the calculation of the projected angles with subscripts 1 and 2 the projection of the carbon atoms C-4, C-5, C-6, C-7 and C-10 and of C-1, C-7, C-8, C-9, C-10, respectively, on a plane perpendicular to C-5—C-9 was used (Figures 1 and 2).

[b] Mean value of the projected angles with subscripts 1 and 2 (see text).

[c] In Ref. 9 only the projected angles with subscript 1 were reported for the MNDO structure of [4]metacyclophane.

Table 2. STO-3G and MNDO calculated carbon–carbon bond lengths and valence angles of [5]- and [4]metacyclophane

	STO-3G		MNDO	
Parameter	[4]	[5][25]	[4][9]	[5][9]
Bond lengths (Å)				
C-5—C-6	1·388	1·390	1·407	1·416
C-6—C-7	1·398	1·392	1·421	1·409
C-7—C-8	1·389	1·392	1·412	1·409
C-8—C-9	1·399	1·390	1·419	1·416
C-9—C-10	1·379	1·381	1·412	1·414
C-10—C-5	1·390	1·381	1·424	1·414
C-9—C-1	1·540	1·527	1·509	1·509
C-1—C-2	1·599	—	1·581	–
C-2—C-3	1·591	—	1·581	—
C-3—C-4	1·594	—	1·577	—
C-4—C-5	1·539	1·527	1·509	1·509
Valence angles (°)				
C-5—C-6—C-7	118·4	119·0	116·8	118·1
C-6—C-7—C-8	118·8	119·9	118·5	118·3
C-7—C-8—C-9	118·8	119·0	118·6	118·4
C-8—C-9—C-10	117·5	118·1	116·9	118·4
C-9—C-10—C-5	116·5	119·7	109·4	111·5
C-10—C-5—C-6	118·1	118·1	119·1	118·6
C-9—C-1—C-2	108·7	106·8	110·4	108·9
C-1—C-2—C-3	122·3	—	124·8	—
C-2—C-3—C-4	122·4	—	124·0	—
C-3—C-4—C-5	104·7	106·8	109·8	108·9

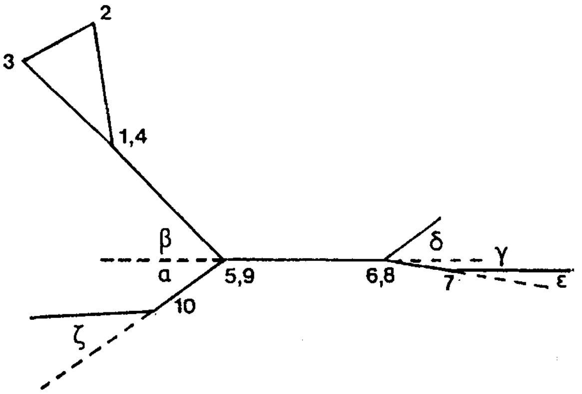

Figure 1. Theoretical molecular structure of [4]metacyclophane based on the STO-3G calculation; side view (projected on a plane perpendicular to C-5—C-9). Note that the Greek letters 1 are only descriptive; for appropriate values, see Table 1 and text

[5]metacyclophane the pyramidalization values (Σ) found in the STO-3G structure were in excellent agreement with those derived from the x-ray structure of 8,11- dichloro[5]metacyclophane.[25,29]

The calculated carbon–carbon bond lengths of the bent benzene ring in the STO-3G structure of [4]metacyclophane vary in the range 1·379–1·399 Å (Figure 2 and Table 2). In comparison, carbon–carbon bond lengths, in the range 1·381–1·392 and 1·386–1·396 Å are calculated at the STO-3G level of theory for [5]metacyclophane and the unstrained reference compound *m*-xylene, respectively.[25] Although some bond alternation is predicted for the carbon–carbon bond lengths of the bent benzene ring of [4]metacyclophane, the modest variation indicates that the benzene ring of [4]metacyclophane still possesses essentially delocalized aromatic carbon–carbon bond lengths; all values fall into the range for highly delocalized compounds.[30] Similar conclusions were previously drawn from the results of MNDO calculations (cf. Table 2, aromatic carbon–carbon lengths; [4]metacyclophane 1·407–1424 Å, [5]metacyclophane 1·409–1·416 Å and *m*-xylene 1·404–1·413 Å, respectively).[9] With the exception of C-10—C-5—C-6, the valence angles of the bent benzene ring in the STO-3G structure of [4]metacyclophane are generally closer to the reference value of 120° (C_{sp^2}—C_{sp^2}—C_{sp^2}) than in the MNDO structure (Figure 2 and Table 2). The largest difference from the reference value is found for the valence angle C-9—C-10—C-5; STO-3G 116·5° and MNDO 109·4°. Although less pronounced, a similar deviation was observed for the corresponding valence angle in

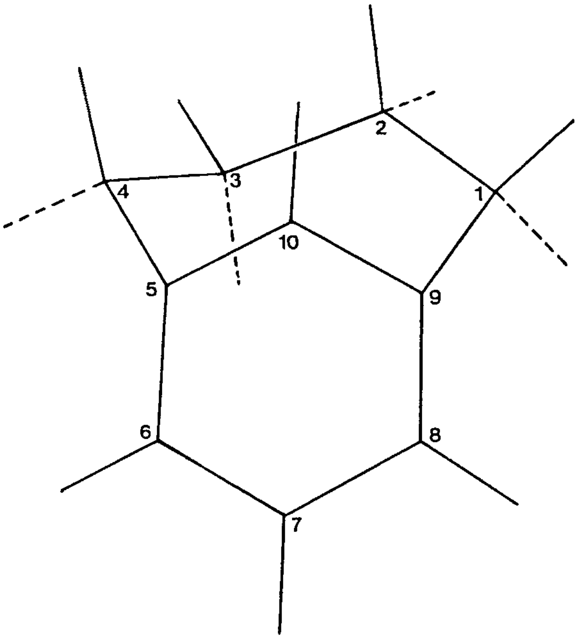

Figure 2. Theoretical molecular structure of [4] metacyclophane based on the STO-3G calculation; top view (projected on the plane defined by C-5, C-8 and C-9)

[5] metacyclophane (STO-3G 119·7° and MNDO 114·5°).[3,9,25] Obviously, the decrease in the C-9—C-10—C-5 angle on going from [5]- to [4] metacyclophane in the STO-3G and MNDO structures is due to the shortening of the oligomethylene bridge. Nevertheless, the bridge appears to exert less compression on the bent benzene ring in the STO-3G structure. This is corroborated by the STO-3G non-bonded carbon–carbon distances C-5—C-9 2·36 and C-6— C-8 2·40 Å (MNDO 2·32 and 2·44 Å, respectively[9]) and the structural parameters of the oligomethylene bridge (Table 2).

As expected, the sp^3-hybridized carbon atoms of the bridge will respond more easily to strain by variations in bond lengths and valence angles. A comparison between the calculated STO-3G and MNDO structure of the oligomethylene bridge of 4] metacyclophane reveals that large deviations occur of both the bond lengths and valence angles from their reference values (bond lengths C_{sp^2}—C_{sp^3} 1·50 Å, C_{sp^3}—C_{sp^3} 1·54 Å and valence angle 109·5°).[31] Extraordinary benzylic- and non-benzylic carbon–carbon bond lengths are calculated in the STO-3G structure (Table 2; benzylic, C-9—C-1 1·540 Å and C-4—C-5 1·539 Å and non-benzylic, C-1—C-2 1·599 Å, C-2—C-3 1·591 Å and C-3—C-4 1.594 Å). They are considerably longer than the corresponding MNDO values, i.e. 1·509, 1·509, 1·581, 1·568 and 1·577 Å, respectively (Table 2).[9] Note, however, that for [5] metacyclophane, a comparison of the STO-3G structural parameters of the bridge with those obtained from the x-ray structure of 8,11-dichloro[5] metacyclophane[29] showed that the bridge carbon–carbon bond lengths are overestimated by 0·01–0·02 Å.[25] In agreement with the available theoretical[9,25] and experimental[29] data for [5] metacyclophanes, the valence angles of the oligomethylene bridge with the exception of the benzylic ones are widened considerably in the STO-3G structure of [4] metacyclophane (Table 2).

STO-3G strain energy of [4] metacyclophane

An estimate of the total strain energy [SE(tot.)] of [4] metacyclophane can be obtained by applying the following homodesmotic reaction for which $\Delta E = -\mathrm{SE(tot.)}$.[32]

$$[4]\,\text{metacyclophane} + 5C_2H_6 \rightarrow m\text{-xylene} + 4C_3H_7$$

From the STO-3G total energies in Table 3 an SE(tot.) of 95·40 kcal mol^{-1} is calculated (1 kcal = 4·184 kJ). To gain insight into the distribution of SE(tot.) over the bent benzene ring [SE(bb.)], a single-point calculation[9,10,22–25] was performed on benzene frozen into the conformation found in [4] metacyclophane. The additional hydrogen atoms were placed at a typical carbon–hydrogen distance (STO-3G, 1·083 Å) in the same direction as the carbon atoms of the bridge C-1 and C-4 (Figure 2).

The STO-3G energy of the bent benzene ring is 76·50 kcal mol^{-1} higher than that of planar benzene itself; thus, SE(bb.) is 76·50 kcal mol^{-1} (Table 3). According to

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

an SE(br.) of 18·90 kcal mol^{-1} is calculated for [4] metacyclophane. Following similar procedures with the MNDO heats of formation (ΔH_f^0) of [4] metacyclophane and related compounds SE(tot.), SE(bb.) and SE(br.) values of 72·3, 57·9 and 14·4 kcal mol^{-1}, respectively are calculated (Table 3). These values are in reasonable agreement with the previously reported data for [4] metacyclophane where SE(tot.) was calculated according to SE(tot.) = ΔH_f^0(MNDO) − ΔH_f^0(group increments) [SE(tot.) = 70·1, SE(bb.) = 57·9 and SE(br.) = 12·2 kcal mol^{-1}].[9] Although it may be argued that, instead of benzene frozen into the conformation found in [4] metacyclophane, the related *m*-xylene would be a better reference compound for the evaluation of SE(bb.), since part of the bond length changes in the aromatic moiety are due to alkyl substitution already present in the equilibrium structure of *m*-xylene compared with benzene, previous MNDO calculations have shown that SE(bb.) = 63·7 kcal mol^{-1} is obtained with *m*-xylene as the reference compound.[9]

Table 3. STO-3G total energies, MNDO heats of formation and strain energy of [4]metacyclophane and related compounds

Compound	E (hartree)[a] (STO-3G)	ΔH_f^0 (kcal mol^{-1}) (MNDO)	SE(tot.) (kcal mol^{-1}) STO-3G	SE(tot.) (kcal mol^{-1}) MNDO	SE(bb.) (kcal mol^{-1}) STO-3G	SE(bb.) (kcal mol^{-1}) MNDO	SE(br.) (kcal mol^{-1}) STO-3G	SE(br.) (kcal mol^{-1}) MNDO
[4]Metacyclophane	−380·922797	77·1[c]	95·40	72·3	76·50	57·9	18·90	14·4
m-Xylene	−305·059968[d]	5·9[c]	—	—	—	—	—	—
Bent benzene[b]	−227·769453	79·1[c]	76·50	57·9	76·50	57·9	—	—
Benzene	−227·891361[d]	21·2[e]	—	—	—	—	—	—
Propane	−116·886422[d]	−24·9[e]	—	—	—	—	—	—
Ethane	−78·306180[d]	−19·7[e]	—	—	—	—	—	—

[a] 1 hartree = 627·50 kcal mol^{-1}.

[b] See text.

[c] Taken from Ref. 9.

[d] Taken from Ref. 25.

[e] Taken from Ref. 8.

This value for SE(bb.) is nearly the same as SE(bb.) = 57·9 kcal mol^{-1} obtained with benzene. Moreover, bent benzenes are commonly used for the determination of SE(bb.) in [*n*]cyclophanes.[9,10,17,22–25] Despite the fact that the STO-3G values are consistently larger, the fractional destabilizations SE(bb.)/SE(tot.) and SE(br)/SE(tot.) are similar at both levels of theory [SE(bb.)/SE(tot.), STO-3G 0·802 and MNDO 0·801]. This indicates that the distributions of SE(tot.) over the bent benzene ring [SE(bb.)] and the oligomethylene bridge [SE(br.)] are essentially the same. As expected, SE(bb.) comprises the largest part of SE(tot.)[9,10,22–25] and SE(bb.) far exceeds the resonance energy of benzene (20–30 kcal mol^{-1}).[30,32] Although this is sometimes taken as evidence to reject the aromatic character of these bent benzenes, our calculations indicate that, despite the severe bending and the occurrence of some bond alternation, the bent benzene ring still possesses carbon–carbon bond lengths in the range for highly delocalized compounds.[30,33] The calculated increase of SE(tot.) on going from [5]- to [4]metacyclophane parallels the difficulties encountered in the experimental identification[11,12] of the latter [SE(tot.), STO-3G (MNDO) [4]metacyclophane 95·40 kcal mol^{-1} (72·3 kcal mol^{-1}) and [5]metacyclophane 57·73 kcal mol^{-1} (46·0 kcal mol^{-1}).[9,25]

CNDO/S–CI electronic transition energies of [4]metacyclophane, [4]paracyclophane and related compounds

It is well established both experimentally[1–4,6,18] and theoretically[18,23,24] that the $S_0 \rightarrow S_1$ transition in the electronic absorption spectrum of [*n*]cyclophanes undergoes a bathochromic shift with decreasing *n*. This indicates that there may be a correlation between the degree of out-of-plane distortion of the benzene ring and the value of the $S_0 \rightarrow S_1$ transition. Recently, it has been shown that also the phosphorescence transition ($T_1 \rightarrow S_0$, ethanol solution at −200 °C) within a series of [*n*]paracyclophanes ($n = 7$–10) is markedly affected by the total degree of out-of-plane distortion of the benzene ring, i.e. the total amount of bending at the 'bow' and 'stern' of the boat-shaped benzene from the original benzene plane (sum of α and γ, Figure 1);[34] a red shift of the $T_1 \rightarrow S_0$ transition concomitant with decreasing *n* was found. Moreover, the value of the $T_1 \rightarrow S_0$ transition was shown to be linearly related to the deviation from planarity of the benzene ring. Since it is expected that, owing to its instability,[11,12,15] the identification of [4]metacyclophane will rely on low-temperature optical spectroscopy, we have calculated its electronic transition energies with CNDO/S–CI[26] using the optimized STO-3G structure as input geometry (cf. Computational Procedures). To assess the reliability of these results, the electronic transition energies of *p*- and *m*-xylene and [5]para-, [4]para- and [5]metacyclophane were also calculated with CNDO/S–CI[26] using optimized STO-3G structures and compared with available experimental data (Table 4). Note that also for [5]meta- and [4]paracyclophane, no calculated electronic transition energies have hitherto been reported. Although it may be argued that CNDO/S–CI is not particularly suited for the calculation of electronic transition energies of these strained compounds, it should be noted that Schaefer and co-workers[23,24] reported DZ SCF calculations of the lowest triplet and excited singlet electronic states of [6]- and [5]paracyclophane. As expected on the basis of their calculation of a singly excited configuration built up from SCF MOs, considerable additive corrections ($S_0 \rightarrow T_1$ 1·30 eV and $S_0 \rightarrow S_1$ 2·28 eV) have to be applied in order to bring the calculated data into agreement with experimental data. In addition, we would like to stress

Table 4. Electronic transition energies, $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$, and oscillator strengths calculated with CNDO/S—CI using optimized STO-3G geometries of *p*- and *m*-xylene and [5]para-, [5]meta-, [4]para- and [4]metacyclophane as input geometries

			Electronic transitions	
Compound	STO-3G structure: reference	Degree of non-planarity[a] (°)	Calc. {nm (eV) [*f*][b]}	Exp.[c] [nm (ev)]
p-Xylene	10	0	264(4·68 [0·007])	268(4·63)
			213(5·80 [0·140])	208(5·97)
			184(6·68 [1·061])	188(6·58)
m-Xylene	25	0	262(4·72 [0·002])	265(4·68)
			211(5·86 [0·039])	211(5·86)
			185(6·68 [1·169])	192(6·46)
[5] Paracyclophane	24	44·8	369(3·35 [0·042])	330(3·75)
			312(3·96 [0·370])	280(4·41)
			226(5·47 [0·606])	—[d]
[5] Metacyclophane	25	33·3	320(3·88 [0·014])	307(4·03)
			251(4·94 [0·006])	238(5·19)
			217(5·71 [0·800])	—[d]
[4] Paracyclophane	10	56·6	456(2·71 [0·031])	375(3·31)[e]
			397(3·11 [0·298])	335(3·70)[e]
			256(4·83 [0·469])	260(4·77)
[4] Metacyclophane	This work	45·2	399(3·11 [0·016])	338(3·67)[f]
				347(3·57)[g]
			296(4·18 [0·009])	284(4·37)[f]
				271(4·57)[g]
			243(5·09 [0·604])	—[d]

[a] Total bending of the boat-shaped benzene from the original benzene plane as found in the optimized STO-3G structures (Figure 1, sum of α and γ). In the case of [4]para-[10] and [4]metacyclophane the sum of $\alpha_{av.}$ and $\gamma_{av.}$ is used (see text).

[b] Oscillator strengths calculated with CNDO/S–CI.

[c] Solvent: for *p*- and *m*-xylene, heptane[39], for [5]paracyclophane, 2-methylbutane,[4] for [5]metacyclophane, cyclohexane,[7] for [4]paracyclophane, ethanol.[6]

[d] Not determined.

[e] Mean values $S_0 \rightarrow S_1$ (370–380 nm) and $S_0 \rightarrow S_2$ (330–340 nm).[6]

[f] Estimated from the linear correlation between the degree of out-of-plane deviation and experimental $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transition energies (see text).

[g] Estimated from the linear correlation between the experimental and calculated values for the electronic transition energies, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ (see text).

that it is our objective to elucidate qualitative relationships which may assist experimental investigations of these intriguing molecules.

A survey of the CNDO/S–CI results shows that both the first ($S_0 \rightarrow S_1$) and second ($S_0 \rightarrow S_2$) electronic transition energies of the reference molecules *p*- and *m*-xylene are in excellent agreement with experiment. However, for the small [*n*]cyclophanes, both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ calculated transitions are red shifted in comparison with available experimental values (Table 4). Furthermore, the deviation between the calculated and experimental data appears to increase concomitant with the degree of non-planarity of the benzene ring, i.e. the total amount of bending at the 'bow' and 'stern' of the boat-shaped benzenes from the original benzene plane (sum of α and γ, Figure 1). Nevertheless, linear correlations are found between the out-of-plane deviation of the boat-shaped benzenes from the original benzene plane taken from STO-3G optimized structures and the CNDO/S–CI calculated $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ electronic transition energies, respectively ($y = A + Bx$; x = degree of non-planarity, y = calculated electronic transition energies in eV:$S_p \rightarrow S_1$, $A = 4{\cdot}75$ eV, $B = -0{\cdot}034$ eV, correlation coefficient = $-0{\cdot}9837$; $S_0 \rightarrow S_2$, $A = 5{\cdot}94$ eV, $B = -0{\cdot}043$ eV, correlation coefficient = $-0{\cdot}9645$; and $S_0 \rightarrow S_3$, $A = 6{\cdot}70$ eV, $B = -0{\cdot}032$ eV, correlation coefficient = $-0{\cdot}9873$). Analogous linear correlations are found between the degree of out-of-plane deviation and the available experimental electronic transition energies ($S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$) in the investigated series ($y = A + Bx$; x = degree of non-planarity, y = experimental electronic transition energies in eV:$S_0 \rightarrow S_1$, $A = 4{\cdot}68$ eV, $B = 0{\cdot}022$ eV, correlation coefficient = $-0{\cdot}9899$; and $S_0 \rightarrow S_2$, $A = 6{\cdot}00$ eV, $B = -0{\cdot}036$ eV, correlation coefficient = $-0{\cdot}9674$). Unfortunately, owing to a lack of experimental data, the assessment of a linear correlation between the degree of non-planarity and the experimental $S_0 \rightarrow S_3$ electronic transition energies within the series was thwarted (cf. Table 4). Obviously, linear correlations are also found between the corresponding calculated and experimental electronic transition energies ($y = A + Bx$; x = calculated electronic transition energies and y = experimental electronic transition energies in eV: $S_0 \rightarrow S_1$, $A = 1{\cdot}47$ eV, $B = 0{\cdot}675$, correlation coefficient = 0·9983; and $S_0 \rightarrow S_2$, $A = 1{\cdot}19$ eV, $B = 0{\cdot}811$, correlation coefficient = 0·9983). Although it should be realized that the latter results may be affected to a certain extent by solvent effects,[35] they indicate that useful estimates for the electronic transition energies of the elusive [4]metacyclophane can be obtained. By applying the linear correlation between either the degree of out-of-plane deviation of the boat-shaped benzenes and the experimental $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transition energies or between the related calculated and experimental electronic transition energies, the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions for [4]metacyclophane are estimated to fall in the range 338–347 nm (3·67–3·57 eV) and 271–284 nm (4·57–4·37 eV), respectively. The reliability of these qualitative linear correlations is further substantiated by the observation that calculation of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transition energies for [8]-, [7]- and [6]paracyclophane using the out-of-plane deviation of the boat-shaped benzenes derived from reported STO-3G structures yields electronic transition energies in reasonable agreement with available experimental {[8]paracyclophane, STO-3G degree of non-planarity 16·8°,[22] $S_0 \rightarrow S_1$ calculated 288 nm (experimental 275 nm)[36] and $S_0 \rightarrow S_2$ calculated 230 nm (experimental 225 nm);[36] [7]paracyclophane, STO-3G degree of non-planarity 25·4°,[22] $S_0 \rightarrow S_1$ calculated 301 nm (experimental 283 nm)[37] and $S_0 \rightarrow S_2$ calculated 244 nm (experimental 245 nm);[37] and [6]paracyclophane, STO-3G degree of non-planarity 34·4°,[23] $S_0 \rightarrow S_1$ calculated 317 nm (experimental 296 nm)[38] and $S_0 \rightarrow S_2$ calculated 261 nm (experimental 253 nm)[38]}. In passing, it should be noted with respect to the calculated oscillator strengths (f) that, owing to a lack of experimental data, we have to refrain from a detailed discussion of their values.

CONCLUSION

The molecular structure of [4]metacyclophane was calculated at the *ab initio* STO-3G level of theory and a genuine minimum was located. In comparison with the previously reported MNDO structure,[9] the bent benzene ring in the STO-3G structure deviates less from planarity and is less geometrically distorted. Despite the distortion from planarity and the occurrence of some bond alternation, the aromatic carbon–carbon bond lengths are in the range for delocalized compounds.[9,25,30] Although the SE(tot.) of [4]metacyclophane is larger at the STO-3G than the MNDO level of theory, the distribution over the bent benzene ring [SE(bb.)] and the oligomethylene bridge [SE(br.)] is the same. A considerable increase in SE(tot.) is calculated on going from [5]- to [4]metacyclophane, which parallels the problems encountered in the characterization of the latter.[11,12] Estimates of the electronic transition energies, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, of [4]metacyclophane calculated with CNDO/S–CI using the optimized STC-3G structure are obtained, which may assist in its experimental identification.

REFERENCES

1. P. M. Keehn and S. M. Rosenfeld, *Cyclophanes*. Academic Press, New York (1983).
2. F. Bickelhaupt and W. H. de Wolf, *Recl. Trav. Chim. Pays-Bas*. **107**, 459 (1988), and references cited therein.
3. F. Bickelhaupt, *Pure Appl. Chem.* **62**, 373 (1990), and references cited therein.
4. L. W. Jenneskens, F. J. J. de Kanter, P. A. Kraakman, L. A. M. Turkenburg, W. E. Koolhaas, W. H. de Wolf, F. Bickelhaupt, Y. Tobe, K. Kakiuchi and Y. Odaira, *J. Am. Chem. Soc.* **107**, 3716 (1985).
5. G. B. M. Kostermans, M. Bobeldijk, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.* **109**, 2471 (1987).
6. T. Tsuji and S. Nishida, *J. Am. Chem. Soc.* **110**, 1257 (1988).
7. J. W. van Straten, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron Lett.* 4667, (1977).
8. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 and 4907 (1977).
9. L. W. Jenneskens, F. J. J. de Kanter, W. H. de Wolf and F. Bickelhaupt, *J. Comput. Chem.* **8**, 1154 (1987), and references cited therein.
10. [4]paracyclophane: L. W. Jenneskens, J. N. Louwen, W. H. de Wolf and F. Bickelhaupt, *J. Phys. Org. Chem.* **3**, 295 (1990).
11. G. B. M. Kostermans, P. van Dansik, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.* **109**, 7887 (1987).
12. G. B. M. Kostermans, P. van Dansik, W. H. de Wolf and F. Bickelhaupt, *J. Org. Chem.* **53**, 4531 (1988).
13. J. W. van Straten, I. J. Landheer, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron Lett.* 4499 (1975).
14. I. J. Landheer, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron Lett.* 2813 (1974).
15. G. B. M. Kostermans, M. Hogenbirk, L. A. M. Turkenburg, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.* **109**, 2855 (1987).
16. W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
17. H. Schmidt, A. Schweig, W. Thiel and M. Jones, Jr., *Chem. Ber.* **111**, 1958 (1978).
18. N. L. Allinger, J. T. Sprague and T. Liljefors, *J. Am. Chem. Soc.* **96**, 5100 (1974).
19. L. Carballeira, J. Casado, E. Gonzales and M. Rios, *J. Chem. Phys.* **77**, 5655 (1982).
20. L. Carballeira, A. J. Pereiras and M. A. Rios, *J. Chem. Phys.* **80**, 4387 (1984).
21. J. T. Sprague, J. C. Tai, Y. Yuh and N. L. Allinger, *J. Comput. Chem.* **8**, 581 (1987).

22. [8]- and [7]paracyclophane: T. J. Lee, J. E. Rice, R. B. Remington and H. F. Schaefer, III, *Chem. Phys. Lett.* **150**, 63 (1988).
23. [6]paracyclophane: T. J. Lee, J. E. Rice, W. D. Allen, R. B. Remington and H. F. Schaefer, III, *Chem. Phys.* **123**, 1 (1988).
24. [5]paracyclophane: J. E. Rice, T. J. Lee, R. B. Remington, W. D. Allen, D. Allen Clabo, and H. F. Schaefer, III, *J. Am. Chem. Soc.* **109**, 2902 (1987).
25. [5]metacyclophane: L. W. Jenneskens, J. N. Louwen and F. Bickelhaupt, *J. Chem. Soc., Perkin Trans.* **2**, 1893 (1989).
26. J. Del Bene and H. H. Jaffé, *J. Chem. Phys.* **48**, 1807 (1968).
27. Gaussian 80: Version D by U. C. Singh and P. A. Kollman taken from the TRIBLE program set: L. Herman, W. Roberson and J. W. ApSimon, *Quart. Chem. Program Exch. Bull.* **7**, 22 (1987).
28. J. W. McIver, Jr and A. Komornicki, *J. Am. Chem. Soc.* **94**, 2625 (1972).
29. L. W. Jenneskens, J. C. Klamer, H. J. R. de Boer, W. H. de Wolf, F. Bickelhaupt and C. Stam, *Angew. Chem.* **96**, 236 (1984).
30. R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.* **107**, 289 (1985), and references cited therein.
31. J. March, *Advanced Organic Chemistry*, pp. 22–26. McGraw–Hill, Kogakusha Tokyo Ltd., (1977).
32. P. George, M. Trachtman, C. W. Bock and A. M. Brett, *J. Chem. Soc. Perkin Trans. 2* 1222 (1976).
33. L. W. Jenneskens, E. N. van Eenige and J. N. Louwen, *New J. Chem.* **16**, 775 (1992).
34. H. Hopff, M. Haase, J. Hunger, W. Tochtermann and M. Zander, *Chem. Phys. Lett.* **127**, 145 (1986).
35. N. L. Turro, *Modern Molecular Photochemistry*. Benjamin/Cummings, Menlo Park, CA (1978).
36. 4-carboxy-[8]paracyclophane: M. G. Newton, T. J. Walter and N. L. Allinger, *J. Am. Chem. Soc.* **95**, 5652 (1973).
37. A. D. Wolf, V. V. Kane, R. H. Levin and M. Jones, Jr, *J. Am. Chem. Soc.* **95**, 1680 (1973).
38. V. V. Kane, A. D. Wolf and M. Jones, Jr, *J. Am. Chem. Soc.* **96**, 2643 (1974).
39. *DMS UV Atlas of Organic Compounds*, Vol. II. Butterworths London (1966).