

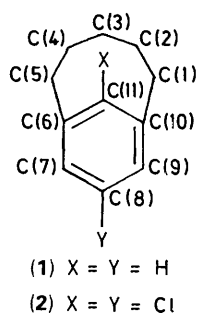
[5]Metacyclophane: *ab initio* STO-3G Molecular Structure and Strain Energy

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The molecular structure and strain energy of [5]metacyclophane (**1**) have been calculated with the *ab initio* STO-3G minimal basis set. The results are compared with previously reported theoretical data of (**1**) obtained with molecular-mechanics calculations (MM) and the semi-empirical MNDO method, and the X-ray structure determination of 8,11-dichloro[5]metacyclophane (**2**). Despite quantitative differences the STO-3G results confirm the MNDO results qualitatively. In comparison with the available experimental data the calculated STO-3G structure of the bent benzene ring shows better agreement. The bent benzene ring in the STO-3G structure possesses essentially delocalized aromatic carbon-carbon bond lengths. Although the calculated STO-3G strain energy [$E_s(\text{tot})$] is larger than either the MM or MNDO value, the distribution of $E_s(\text{tot})$ over the bent benzene ring [$E_s(\text{bb})$] and the oligomethylene bridge [$E_s(\text{br})$] is similar.

Recently, two papers have been published in which [n]metacyclophanes with $n = 10-5$ and $n = 7-4$ were studied theoretically with molecular mechanics (MM) and MNDO, respectively.^{1,2} The primary aim of both investigations was to gain insight into the strain energy of these intriguing compounds and its effect on geometry, aromaticity, and the distribution of strain over the bent benzene ring and the oligomethylene bridge as a function of n . In comparison with the limited available experimental data, MNDO especially gave a reasonable representation of the [n]metacyclophanes.³ Nevertheless, several anomalies were observed between the MNDO calculated and experimental structure of 8,11-dichloro[5]metacyclophane (**2**).^{2,4,5} The latter is a crystalline derivative of [5]metacyclophane (**1**),⁶ the smallest stable representative of its class, for which an X-ray structure has been determined.⁴



For example, the deviation from planarity of the bent benzene ring at the 'bow' of the molecule [Figure 1 and Table 1; MNDO (*X-ray*) $\alpha = 36.2^\circ$ (26.8°)] and the aromatic carbon-carbon bond lengths [Figure 2 and Table 2; average value MNDO (*X-ray*) 1.415 Å (1.393 Å)] are overestimated. On the other hand, the valence angle C(6)-C(11)-C(10) is underestimated (see diagram above, Figure 2, and Table 2; C(6)-C(11)-C(10) [MNDO (*X-ray*) 114.8° (118.7°)]. Recently, Schaefer and co-workers have shown for the related [n]paracyclophanes that *ab initio* calculations with the STO-3G minimal basis set⁷ of [8]-, [7]-, and [6]-paracyclophane give structures in better agreement with experiment than those obtained with MM and MNDO, respectively.^{8,9} Since we are not aware of any reported *ab initio* calculations of [n]metacyclophanes, we have reinvestigated [5]metacyclophane (**1**). Here we report the molecular structure, strain energy and its distribution over the bent

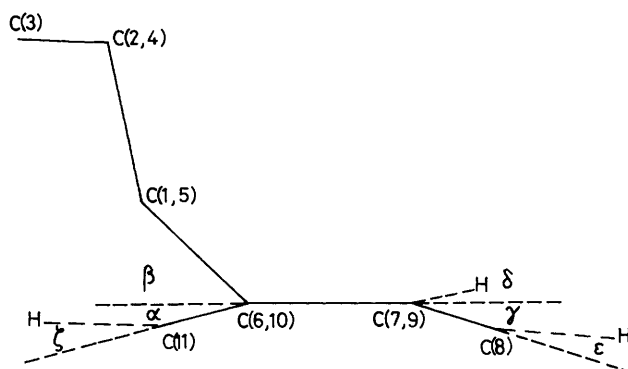


Figure 1. STO-3G Molecular structure of [5]metacyclophane (**1**); side view.

benzene ring and the oligomethylene bridge of [5]metacyclophane (**1**) calculated with the STO-3G minimal basis set⁷ as implemented¹⁰ in GAUSSIAN 80.

Discussion

ab initio STO-3G Molecular Structure of [5]Metacyclophane (**1**).—The molecular structure of [5]metacyclophane (**1**) was optimized without any geometrical constraints, using the MNDO structure² as the starting geometry. The gradients were smaller than 1×10^{-4} hartree bohr⁻¹ and the optimized STO-3G structure of (**1**) was shown to be a genuine minimum, *i.e.* all force constants were positive.¹¹ Pertinent results of the STO-3G calculations are presented in Figures 1 and 2 and in Tables 1, 2, and 3, respectively. In agreement with the previously reported theoretical data^{1,2} and the X-ray structure determination of (**2**),⁴ the STO-3G structure of [5]metacyclophane (**1**) possesses C_s symmetry and the bent benzene ring has an unsymmetrical boat-shape (Figure 1).

The projected angle α , which is a measure of the deviation from planarity of the bent benzene ring at the 'bow' of the molecule takes the value 22.2° in the STO-3G structure (Figure 1 and Table 1). In comparison with the MM and MNDO value of α , 30.4° and 32.5°, respectively, the STO-3G structure is much less bent. Although a precise comparison between theory

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Table 1. Calculated projected angles of [5]metacyclophane (1).^a

Angle/°	(1)			(2)	
	STO-3G	MNDO ^b	MM ^c	X-ray ^d	MNDO ^b
α	22.2	32.5	30.4	26.8	36.2
β	40.9	43.1	—	48.0	43.8
γ	11.1	9.2	5.8	12.0	10.6
δ	17.9	7.7	—	—	8.5
ϵ	9.4	4.6	—	7.8	5.1
ζ	19.5	13.9	-3.55	13.8	6.8

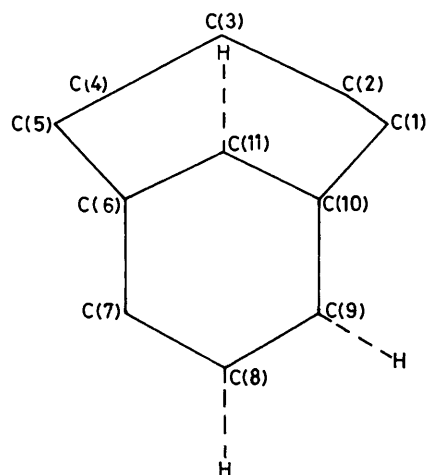
^a For a definition of the projected angles see Figure 1. ^b Taken from ref. 2. ^c Taken from ref. 1. ^d Taken from ref. 4.

Table 2. Calculated structural parameters of [5]metacyclophane (1).^a

Bond lengths/Å	(1)			(2)	
	STO-3G	MNDO ^b	MM ^c	X-ray ^d	MNDO ^b
C(6)–C(11)	1.381	1.414	1.366	1.391	1.421
C(6)–C(7)	1.390	1.416	1.385	1.400	1.414
C(7)–C(8)	1.392	1.409	1.395	1.389	1.410
C(1)–C(10)	1.527	1.509	1.486	1.506	1.510
C(1)–C(2)	1.579	1.566	—	1.569	1.567
C(2)–C(3)	1.581	1.559	1.571	1.566	1.556
Valence angles/°	(1)			(2)	
	STO-3G	MNDO ^b	MM ^c	X-ray ^d	MNDO ^b
C(11)–C(6)–C(7)	118.1	118.3	119.9	117.4	116.7
C(6)–C(7)–C(8)	119.0	118.4	—	118.8	118.4
C(7)–C(8)–C(9)	119.9	120.0	119.1	120.3	120.1
C(6)–C(11)–C(10)	119.7	114.5	114.6	118.7	114.8
C(10)–C(1)–C(2)	106.8	108.9	108.5	104.7	108.9
C(1)–C(2)–C(3)	121.2	121.4	118.5	121.9	122.1
C(2)–C(3)–C(4)	121.5	122.3	118.4	122.2	121.9

^a For numbering see Figure 2. ^b Taken from ref. 2. ^c Taken from ref. 1. ^d Taken from ref. 4.

and experiment is not possible without the direct calculation of 8,11-dichloro[5]metacyclophane (2), the STO-3G value agrees best. Similar observations, though less pronounced apply to the projected angle γ at the 'stern' of the molecule (Figure 1 and Table 1). All substituents present on the benzene ring are predicted to deflect to the convex side; they are located on the same side as the oligomethylene bridge (Figure 1 and Table 1; β , δ , ϵ , and ζ , respectively). Similar deflections were observed for the substituents of (1) and (2) in the MNDO structures² and the X-ray structure.⁴ However, MM predicted incorrectly for (1) a deflection in the opposite direction for the hydrogen atom at C(11) (Table 1; $\zeta = -3.55^\circ$).¹ Although the results of the STO-3G and MNDO calculations are in qualitative agreement with the X-ray structure determination of (2), quantitative deviations are found for the absolute values of β , δ , ϵ , and ζ , respectively (Table 1). It is worth mentioning that MNDO calculations on a series of derivatives of (1), bearing different substituents at C(11), indicated that the angles α , β , and ζ are interdependent.² Therefore, we have to refrain from further discussion in the absence of further experimental data. The calculated direction of deflection of the substituents is in agreement with the optimization of p-orbital alignment in the bent benzene ring.^{1,2} An inspection of the sum of valence angles of the latter reveals that pyrimidalization (rehybridization) occurs at the bridgehead carbon atoms, C(6) and C(10), and, especially, at the carbon atom C(11) [Figure 2; sum of valence angles Σ , STO-3G (MNDO); C(8) $\Sigma = 359.1^\circ$ (359.8°), C(7) $\Sigma = 359.8^\circ$ (359.9°), C(6) $\Sigma = 355.0^\circ$ (356.5°), and C(11) $\Sigma = 356.2^\circ$ (357.9°)]. The STO-3G values of Σ show good agreement with

**Figure 2.** STO-3G Molecular structure of [5]metacyclophane (1); top view.

those derived from the X-ray structure of 8,11-dichloro[5]metacyclophane (2) [C(8) $\Sigma = 359.3^\circ$, C(7) $\Sigma = 359.1^\circ$, C(6) $\Sigma = 354.0^\circ$, and C(11) $\Sigma = 358.1^\circ$].⁴

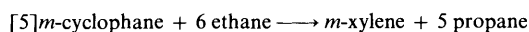
The calculated carbon-carbon bond lengths of the bent benzene ring of [5]metacyclophane (1) in the STO-3G structure vary in the range 1.381–1.392 Å (Figure 2 and Table 2). Only a modest variation is observed from the STO-3G calculated carbon-carbon bond lengths of the unstrained reference compound *m*-xylene (1.386–1.396 Å). Thus, in agreement with the available theoretical^{1,2} and experimental^{4,13} data the bent benzene ring of (1) in the STO-3G structure possesses essentially delocalized aromatic carbon-carbon bond lengths. A survey of the aromatic carbon-carbon bond lengths of (1) obtained at different levels of theory shows that the STO-3G values agree best with those found in the X-ray structure of (2) [Table 2, average value; (1), STO-3G 1.388 Å, MNDO 1.413 Å, MM 1.382 Å and (2), X-ray 1.393 Å and MNDO 1.415 Å, respectively].^{1,2,4} All valence angles of the bent benzene ring in the STO-3G structure of (1) are close to 120° (Table 2). Noteworthy is the value of the angle C(6)–C(11)–C(10) at the 'bow' of the molecule, which in comparison with the available experimental data was underestimated by the MM and MNDO calculations [Table 2, C(6)–C(11)–C(10); STO-3G 119.7°, MNDO 114.5°, MM 114.6° and (2), X-ray 118.7° and MNDO 114.8°].^{2,4} Apparently, in the STO-3G structure of (1) the oligomethylene bridge exerts less compression on the bent benzene ring of [5]metacyclophane (1). This is supported by the STO-3G calculated non-bonded distances between C(6)–C(10) (2.39 Å) and C(7)–C(9) (2.41 Å) (1) [MNDO C(6)–C(10) 2.38 Å and C(7)–C(9) 2.44 Å and (2), X-ray C(6)–C(10) 2.39 Å and C(7)–C(9) 2.41 Å],² and the calculated structural parameters of the bridge (Table 2). The less rigid sp³-hybridized carbon atoms will respond more easily to strain by variation in bond lengths and valence angles from their reference values (bond lengths, C_{sp²}–C_{sp³} 1.50 Å, C_{sp³}–C_{sp³} 1.54 Å and valence angle 109.5°, respectively).¹⁴ Substantial deviations are calculated for both the bond lengths and valence angles (Table 2). In comparison with the MM and MNDO structure of (1) and the X-ray structure of (2) STO-3G overestimates the aliphatic carbon-carbon bond lengths by 0.01–0.02 Å. The valence angles of the oligomethylene bridge, except the benzylic one, in the STO-3G, MNDO and MM structure of (1), respectively, are predicted to widen considerably (Figure 2 and Table 2). Although both the STO-3G and MNDO calculated values are in reasonable agreement with those found in the X-ray structure of (2), the former are slightly better.

Table 3. STO-3G total energies (E), MNDO heats of formation (ΔH_f°) and strain energies (E_s) of [5]metacyclophane (**1**) and related compounds.

Compound	STO-3G		MNDO		
	E^a	$\Delta H_f^{b,c}$	$E_s(\text{tot})^b$	$E_s(\text{bb})^b$	$E_s(\text{br})^b$
[5]metacyclophane (1)	-419.563 000	45.6	57.73 (46.0) ^f	39.60 (33.3)	18.13 (12.7)
<i>m</i> -xylene	-305.059 968	5.9	—	—	—
bent benzene ^c	-227.828 258	54.5	39.60 (33.3)	39.60 (33.3)	—
benzene	-227.891 361 ^d	21.2 ^e	—	—	—
propane	-116.886 422 ^d	-24.9 ^e	—	—	—
ethane	-78.306 180 ^d	-19.7 ^e	—	—	—

^a In hartrees (1 hartree = 627.50 kcal mol⁻¹). ^b In kcal mol⁻¹. ^c cf. Text. ^d Taken from ref. 17. ^e Taken from ref. 18. ^f With MM an $E_s(\text{tot}) = 43.4$ kcal mol⁻¹ is calculated for [5]metacyclophane (**1**).¹

Strain Energy of [5]Metacyclophane (1).—An estimate of the strain energy $E_s(\text{tot})$ of [5]metacyclophane (**1**) can be obtained by applying the following homodesmotic reaction.¹⁵



Scheme.

For the latter $\Delta E = -E_s(\text{tot})$. From the STO-3G total energies a $E_s(\text{tot}) = 57.73$ kcal mol⁻¹ is calculated for [5]metacyclophane (**1**) (Table 3).^{*} To gain insight into the distribution of $E_s(\text{tot})$ over the bent benzene ring [$E_s(\text{bb})$] and the oligomethylene bridge [$E_s(\text{br})$] we have performed a single-point STO-3G calculation on the benzene ring frozen in the conformation present in (**1**). The additional hydrogen atoms were placed at a typical aromatic carbon-hydrogen distance (1.083 Å) in the same direction as the carbon atoms C(1) and C(5) of the oligomethylene bridge. An $E_s(\text{bb})$ value of 39.60 kcal mol⁻¹ was calculated (Table 3). According to

$$E_s(\text{tot}) = E_s(\text{bb}) + E_s(\text{br}) \quad (1)$$

an $E_s(\text{br})$ value of 18.13 kcal mol⁻¹ is obtained. By following the same procedure with the MNDO-calculated heats of formation (ΔH_f°) of [5]metacyclophane (**1**) and related compounds $E_s(\text{tot})$, $E_s(\text{bb})$, and $E_s(\text{br})$ values of 46.0, 33.3, and 12.7 kcal mol⁻¹, respectively were calculated cf. ref. 2). With MM an $E_s(\text{tot})$ value of 43.4 kcal mol⁻¹ for (**1**) was obtained.¹ However, no analysis of the distribution of the $E_s(\text{tot})$ was executed (Table 3). Although the STO-3G value of $E_s(\text{tot})$ is larger, the ratios between $E_s(\text{bb})/E_s(\text{tot})$ and $E_s(\text{br})/E_s(\text{tot})$ are nearly the same at the STO-3G and MNDO level of theory (**1**), STO-3G (MNDO); $E_s(\text{bb})/E_s(\text{tot})$ 0.69 (0.72). This indicates that, despite differences in absolute values, the distribution of $E_s(\text{tot})$ of [5]metacyclophane (**1**) over the bent benzene ring and the oligomethylene bridge is similar. General considerations indicate that $E_s(\text{bb})$ comprises the largest part of $E_s(\text{tot})$. Intriguingly, $E_s(\text{bb})$ exceeds the resonance energy of benzene (20–30 kcal mol⁻¹).¹⁶ Although this is sometimes taken as evidence against the aromatic character of [5]metacyclophane (**1**), our calculations clearly indicate that in the STO-3G structure the bent benzene ring against shows no tendency towards localization.²

Conclusions

The molecular structure of [5]metacyclophane (**1**) was calculated at the *ab initio* STO-3G level of theory; a genuine minimum was located. The bent benzene ring deviates less from

planarity in the STO-3G structure; the projected angles α and γ show better agreement with the available experimental data. The same applies to the STO-3G calculated aromatic carbon-carbon bond lengths and valence angles. Although $E_s(\text{tot})$ of [5]metacyclophane (**1**) is larger at the STO-3G level, the distribution of $E_s(\text{tot})$ over the bent benzene ring [$E_s(\text{bb})$] and the oligomethylene bridge [$E_s(\text{br})$] is similar in the STO-3G and MNDO structure.²

Acknowledgements

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* 1 cal = 4.1868 J.