

On the Importance of Electron Correlation Effects for the π - π Interactions in Cyclophanes

Stefan Grimme*^[a]

Abstract: Correlated ab initio quantum chemical methods based on second-order perturbation theory and density functional theory (DFT) together with large atomic orbital (AO) basis sets are used to calculate the structures of four cyclophanes with two aromatic rings and one sulphur-containing phane with one aromatic ring. The calculated geometrical data for [2.2]paracyclophane, cyclophane (superphane), 8,16-dimethyl[2.2]metacyclophane, 16-methyl[2.2]-metaparacyclophane, and 2,6,15-trithia[3^{4,10}][7]metacyclophane are compared to experimental data from X-ray crystal structure determinations. In all cases, very accurate theoretical predictions are obtained from the recently developed spin-component-scaled MP2 (SCS-MP2) method, in which the devi-

ations are within the experimental accuracy and expected crystal-packing or vibrational effects. Especially the interring distances, which are determined by a detailed balance between attractive van der Waals (dispersive) and repulsive (Pauli) contributions, are very sensitive to the level of theory employed. While standard MP2 theory in general overestimates the dispersive interactions (π - π correlations) between the two aromatic rings leading to too short distances (between 3 and 8 pm), the opposite is observed for DFT methods

(errors up to 15 pm). This indicates that an explicit account of dispersive-type electron correlation effects between the clamped aromatic units is essential for a quantitative description of cyclophane structures. In order to distinguish these effects from “normal” van der Waals interactions, the term “overlap-dispersive” interaction may be employed. The popular B3LYP hybrid density functional offers no advantage over the pure PBE functional that at least qualitatively accounts for some of the dispersive effects. The use of properly polarized AO basis sets of at least valence-triple- ζ quality is strongly recommended to obtain quantitative predictions with traditional wave function methods.

Keywords: ab initio calculations • cyclophanes • density functional calculations • pi interactions • stacking interactions

Introduction

Cyclophanes, in which more than two atoms of an aromatic ring are incorporated into a larger ring system, provide a fine vehicle for the study of molecular strain. The questions “how bent can a benzene ring be” and “how will two benzene rings behave when compressed together below their typical van der Waals distance” represent challenges in molecular design, synthesis, and spectroscopy.^[1–3] The study of close contacts of aromatic units is furthermore of fundamental importance in many supramolecular structures and also in biochemistry, for example, for the stacking of base pairs in DNA.^[4–6] The study of these so-called π - π interactions in the intramolecular situation of the cyclophanes may provide

detailed insights and understanding of molecular structure that can also be used for intermolecular cases.

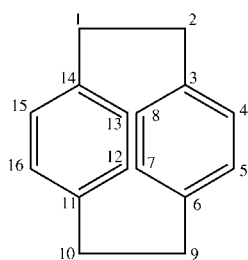
Theoretically, the attractive part of π - π interactions between aromatic molecules/units contains dominating van der Waals (VDW, dispersion) and weaker electrostatic (ES, mainly quadrupole–quadrupole) contributions. At shorter distances, exchange–repulsion (ER) as a result of the Pauli principle dominates the interaction energy. While ER and ES effects can already be described at a mean-field (i.e., Hartree–Fock) level of theory, the VDW part is a pure electron correlation (EC) effect. In the framework of standard ab initio wavefunction theory,^[7] it can be described by double excitations between occupied and virtual orbitals of the supermolecule (coupled monomer single excitations). Although the nowadays most widely used theoretical approach to molecular structure, density functional theory (DFT),^[8,9] includes EC in an approximate manner, it is now clear that almost all standard density functionals are unable to describe dispersive interactions (see, for example, reference [10] and references therein). Probably the earliest DFT study which reported significant overestimations of the

[a] Prof. Dr. S. Grimme
Theoretische Organische Chemie
Organisch-Chemisches Institut der Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49)251-83-33412
E-mail: grimmes@uni-muenster.de

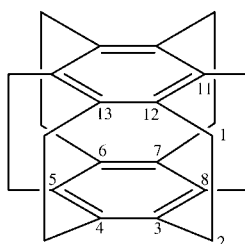
inter-ring distances (IRD) in cyclophanes dates back to the mid 1990s^[11] (see also references [12,13]). Errors as large as 10 pm have been reported although the connection to the “dispersion problem” of DFT was not recognized at that time.

This work represents the first systematic study of typical cyclophane structures with modern quantum chemical methods, together with the use of extended atomic orbital (AO) basis sets. Prior to the advent of DFT, second-order Møller–Plesset perturbation theory (MP2)^[14,15] was the simplest and least expensive way of incorporating EC effects in ab initio electronic structure calculations. It still has certain advantages over DFT, for example, when dispersion forces or charge-transfer processes are important. For the VDW interactions of larger π systems, however, it is now well known that standard MP2 overestimates the binding energies and underestimates intermolecular equilibrium distances (see for example, reference [16] and references therein). It will be shown here that a recently introduced improved version of MP2 (termed SCS-MP2)^[17] provides uniformly very accurate cyclophane structures that are within the error bars of experimental X-ray crystal structure determinations. The two common density functionals B3LYP^[18,19] and PBE^[20] will be used for comparison.

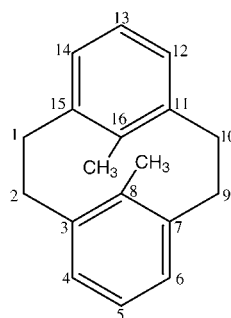
Besides the most prominent structure [2.2]paracyclophane (**1**), a metacyclophane (8,16-dimethyl[2.2]metacyclophane (**3**)) and a metaparacyclophane (**4**) with methyl groups in sterically demanding positions are investigated. The most strained [2₆]cyclophane (**2**, superphane) is considered, because of its extremely short inter-ring contacts. The 2,6,15-trithia[3^{4,10}][7]metacyclophane (**5**) is an example for a phane with hetero (sulfur) atoms in the bridges and a close C–H ring contact.



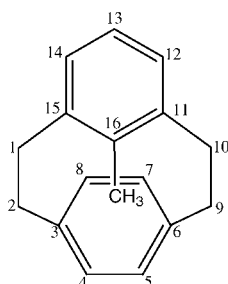
1 (D_2)



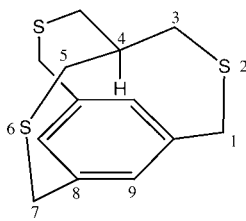
2 (D_{6h})



3 (C_{2h})



4 (C_s)



5 (C_3)

Computational methods

All calculations were performed with the TURBOMOLE suite of programs.^[21] In all SCS-MP2 and MP2 treatments, the resolution-of-the-identity (RI) approximation^[22–26] (also called “density fitting”) for the two-electron integrals was employed; this yielded errors for equilibrium bond lengths of less than 0.05 pm (for a parallel RI-MP2 energy implementation see reference [27]). The RI auxiliary basis sets were taken from references [28,29], in which they were optimized for the TZV and Dunning’s cc-pVxZ AO basis sets, respectively.

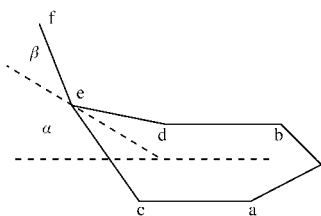
In two recent papers^[17,30] it could be shown that a simple modification of the standard MP2 scheme leads to dramatic improvements in accuracy. The new method, termed spin-component scaled (SCS) MP2 is based on a separate scaling of the second-order parallel ($\alpha\alpha + \beta\beta$) and antiparallel ($\alpha\beta$) spin pair correlation energies. The procedure effectively reduces many outliers observed in standard MP2 calculations and seems to be a robust and valuable quantum chemical tool of general use. For energetic problems, we have already demonstrated in further applications for DNA base tautomers^[31], pericyclic transition states,^[32] and fluorobenzene acidities^[33] the success of the new model. Improvements for the calculation of the equilibrium structures of molecules have been demonstrated in reference [34].

In all correlation treatments only valence electrons were considered (frozen core). Gaussian AO basis sets of valence triple- ζ quality (TZV[35], i.e., C[5s3p], S[5s4p] H[3s]) with a (2df/2p) set of polarization/correlation functions on non-hydrogen and hydrogen atoms, respectively, were used. The issue of the quality of the AO basis set employed is of critical importance for the study of weak interactions. Small (very incomplete) sets tend to provide too short non-bonded contacts due to basis set superposition error (BSSE). On the other hand, small basis sets are not able to provide accurate polarizabilities of the fragments; this leads to too weak VDW attractions. For AO basis sets of intermediate quality (valence-double- ζ , for example, 6–31G*) both effects (of opposite sign) may accidentally cancel, such that for some systems relatively good predictions can be obtained. However, for systematic studies of a variety of systems, in general it is not recommended to rely on error compensation and thus, in this study large AO basis sets which yielded results close to the limit were employed.

To illustrate this point in more detail, a basis set convergence study for the two inter-ring distances (IRD) C3–C14 and C4–C13 in the [2.2]paracyclophane were performed at both the MP2 and DFT-B3LYP levels.

Dunning’s correlation-consistent cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ basis sets^[36,37] were used for this purpose. As expected, the variations of the calculated distances are small (<0.5 pm) at the B3LYP level. With MP2 we obtained 276.4, 274.9, 274.8 pm and 306.3, 304.8, 304.3 pm, respectively, with the three AO basis sets for the two parameters. These data show that properly polarized triple- ζ basis sets are necessary in explicitly correlated calculations. With our standard TZV(2df,2p) set values of 274.9 and 304.8 pm are obtained for C3–C14 and C4–C13, respectively; these values are the same as those obtained with the larger cc-pVTZ set. The effect of the diffuse (aug) functions seems to be also relatively small, so that we can conclude that these sensitive geometrical parameters are within 0.5–1 pm of the basis set limiting values. Considering the estimated experimental accuracy of about 1 pm for these quantities, this seems to be sufficient to draw general conclusions about the performance of the different methods.

The experimental data for **2–5** were obtained from the structures taken from the Cambridge Crystallographic Database.^[38] The data of **1** were taken from a recently re-measured structure which will be published in detail separately.^[39] Beside all important bond lengths between non-hydrogen atoms and the IRD, the benzene ring deformation angles (RDA) α and β (see Scheme 1) were considered.



Scheme 1. Definition of the benzene ring deformation angles (RDA) α and β . α is the angle between the midpoints a–b, c–d, and the atom e. β is the angle between the the midpoints c–d and the atoms e and f.

Results

[2.2]Paracyclophane: The [2.2]paracyclophane molecule is the most prominent, but also structurally the most difficult phane considered here. The first X-ray structure of **1** indicated a rigid, face-to-face molecule with D_{2h} symmetry.^[40] A later refinement revealed that at 93 K the substance equilibrates between two structures in which the methylene bridges are slightly de-eclipsed.^[41] The most recent X-ray structure of **1** determined at 19 K clearly shows a twisted structure with D_2 symmetry^[42] and a dihedral angle C(Ar)–C–C(Ar) of $\phi = 12.6^\circ$.^[39] Phane **1** is the only molecule in this study for which different theoretical treatments predict qualitatively different structures. At the DFT-B3LYP/TZV(2df,2p) level, a minimum with D_{2h} symmetry is obtained that also prevails with larger AO basis sets. Previous B3LYP/4–31G(d) calculations of Walden and Glatzhofer,^[43] which gave a slightly twisted geometry ($\phi = 3.9^\circ$), seem to suffer from basis set incompleteness and are thus not decisive. The MP2/6–31G(d) calculations performed in 1998 by Henseler and Hohlneicher^[44] gave $\phi = 21.8^\circ$, which is in reasonable agreement with the MP2 data reported here. With larger basis sets, MP2 calculations yield a twist angle around 19° and SCS-MP2/TZV(2df,2p) reduces this value to 17.6° (see Figure 1 and Table 1).

The very good agreement of the DFT-PBE result with experiment ($\phi = 10.7$ versus 12.6° (exptl), see Table 1) must be considered as fortuitous, because the other geometrical parameters at this level are less accurate than those from, for example, SCS-MP2. This twist angle seems to be relative sensitive to the experimental measurement conditions as can be seen from the value of 16.1° obtained in the older X-ray study.^[41] Considering furthermore the tiny D_2 – D_{2h} barrier (double-minimum potential) of about $0.2 \text{ kcal mol}^{-1}$ (SCS-MP2/cc-pVTZ), strong vibrational (anharmonic) effects on this parameter are expected, such that the deviation of the SCS-MP2 result does not seem alarming. All other structural details are very accurately predicted by SCS-MP2, as indicated by the low mean absolute deviation (MAD) of

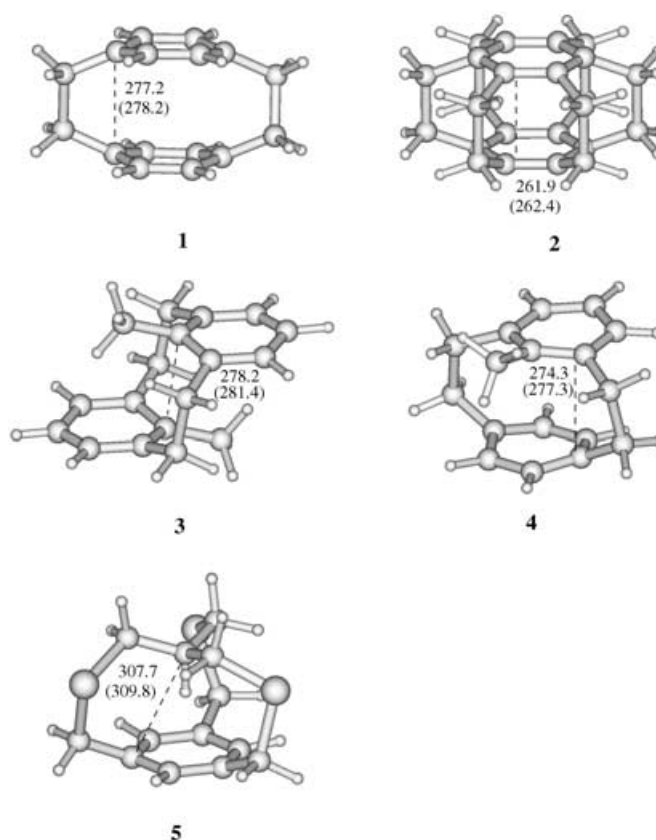


Figure 1. Optimized structures of the investigated cyclophanes (SCS-MP2/TZV(2df,2p)). Theoretical and experimental (in parentheses) shortest inter-ring distances are given in pm.

Table 1. Comparison of experimental^[a] and calculated^[b] structural parameters of [2.2]paracyclophane (**1**). Distances r are given in pm, the deformation angles α and β in degrees. The mean deviation [$\text{MD} = 1/N \sum r(\text{exptl}) - r(\text{calcd})$] and mean absolute deviation [$\text{MAD} = 1/N \sum |r(\text{exptl}) - r(\text{calcd})|$] are given for all distances.

	Exptl	Method			
		SCS-MP2	MP2	DFT-B3LYP	DFT-PBE
r_{C1C2}	159.3	159.4	158.9	161.1	160.7
r_{C2C3}	150.8	150.6	150.3	151.0	151.0
r_{C3C4}	139.9	140.1	140.0	139.7	140.4
r_{C3C8}	139.9	140.0	139.9	139.7	140.3
r_{C4C5}	139.6	139.4	139.3	138.9	139.5
r_{C3C14}	278.2	277.2	274.9	282.7	281.4
r_{C4C13}	309.7	308.0	304.8	315.6	314.3
ϕ ^[c]	12.6	17.6	18.7	0.0	10.7
α	12.5	12.2	11.8	13.0	12.9
β	11.0	11.5	11.6	10.8	10.9
MD		0.4	1.3	–1.6	–1.5
MAD		0.5	1.4	1.9	1.5

[a] X-ray data (average of symmetry equivalent parameters) at 19 K taken from reference [39]. [b] TZV(2df,2p) AO basis set. [c] Dihedral angle C14 C1–C2–C3 in degrees.

0.5 pm and errors < 1 pm for the IRD and $< 0.5^\circ$ for the ring deformation angles (RDA).

The MP2 and DFT structures are significantly less accurate. At the MP2 level the IRD are underestimated by about 5 pm, while overestimations between 4 and 6 pm are obtained from both DFT treatments. Note also, that the sp^3 – sp^3 bridging bond lengths are too long (by 1–2 pm) at the

DFT level. When comparing the two density functionals, it turns out that PBE at least qualitatively predicts a correct (twisted) structure for **1** and that also the MAD for the B3LYP functional is larger. Thus, we can conclude that the overall accuracy of the three methods is $\text{SCS-MP2} > \text{MP2} > \text{DFT-PBE} > \text{DFT-B3LYP}$.

[2₆]Cyclophane: The superphane is the most strained molecule of the cyclophanes investigated. In the D_{6h} symmetry, which is found as a minimum in the calculations and also observed in the crystal, there are six fully eclipsed ethano bridges, short H...H interbridge contacts, and an unfavorable face-to-face arrangement of the two benzene rings (the analogous D_{6h} structure of the benzene dimer is not a minimum; see, for example, reference [44]). The experimental IRD of 262.4 pm is the shortest and the angle β (19.7°) is the largest of all systems, indicating considerable strain. Somewhat surprisingly, the CC-bridge bond length is shorter than in **1** (158 versus 159.3 pm); this is not corroborated by the theoretical treatments, which yield almost the same value (within ± 0.5 – 0.8 pm) for **2** and **1**. The question of whether this qualitatively different picture results from vibrational (experimental data refer to r_0 instead of the calculated r_e values) or packing effects cannot be answered at present. Deficiencies of the theoretical treatment (especially SCS-MP2) seem, however, unlikely considering the overall accuracy for the different cyclophane structures considered. Again, the SCS-MP2 structure is in very good agreement with the experimental data (MAD = 0.7 pm, see Table 2).

Table 2. Comparison of experimental^[a] and calculated^[b] structural parameters of the superphane (**2**). Distances r are given in pm, the deformation angle β in degrees. The mean deviation [$\text{MD} = 1/N \sum (r(\text{exptl}) - r(\text{calcd}))$] and mean absolute deviation [$\text{MAD} = 1/N \sum |r(\text{exptl}) - r(\text{calcd})|$] are given for all distances.

	Exptl	Method			
		SCS-MP2	MP2	DFT-B3LYP	DFT-PBE
r_{C1C2}	158.0	159.6	159.4	160.3	160.2
r_{C2C3}	151.7	151.5	150.7	151.9	151.7
r_{C3C4}	140.6	141.2	141.2	140.9	141.5
r_{C3C12}	262.4	261.9	259.8	265.6	264.4
β	19.7	19.7	19.5	21.3	21.1
MD		-0.4	0.4	-1.5	-1.3
MAD		0.7	1.4	1.5	1.3

[a] X-ray data (average of symmetry equivalent parameters) taken from reference [50]. [b] TZV(2df,2p) AO basis set.

The largest deviation of 1.6 pm occurs for the bridge bond length. With MP2 the C(ar)–CH₂ bond lengths and the IRD are too short by 1 pm and 2.6 pm, respectively. The errors from both DFT treatments are qualitatively similar as for **1**, that is, too large IRD and RDA, although the errors are generally smaller. This may be attributed to the more rigid structure of **2**, which is (relative to **1**) dominated more by bonded interactions. The overall accuracy of the three methods is $\text{SCS-MP2} \gg \text{DFT-PBE} \approx \text{MP2} > \text{DFT-B3LYP}$.

8,16-Dimethyl[2.2]metacyclophane: The two benzene rings in **3** are displaced stepwise, in a manner typical for metacyclophanes, and the benzene rings are distorted asymmetrically to a boat shape in order to avoid too close mutual contact (see Figure 1). At first glance, the methyl groups seem to introduce additional repulsive interactions because they are located almost exactly above the center of the other aromatic ring. As can be seen from the data in Table 3, howev-

Table 3. Comparison of experimental^[a] and calculated^[b] structural parameters of 8,16-dimethyl[2.2]metacyclophane (**3**). Distances r are given in pm, the deformation angles α and β (methyl-substituted side) in degrees. The mean deviation [$\text{MD} = 1/N \sum (r(\text{exptl}) - r(\text{calcd}))$] and mean absolute deviation [$\text{MAD} = 1/N \sum |r(\text{exptl}) - r(\text{calcd})|$] are given for all distances.

	Exptl	Method			
		SCS-MP2	MP2	DFT-B3LYP	DFT-PBE
r_{C1C2}	157.1	157.2	156.9	158.3	158.3
r_{C2C3}	152.0	151.1	150.4	151.4	151.2
r_{C3C4}	139.5	140.0	140.0	139.6	140.3
r_{C4C5}	139.2	139.5	139.5	139.1	139.7
r_{C3C8}	141.3	141.1	141.1	141.0	141.7
r_{C3C15}	299.5	298.6	296.2	304.6	303.0
r_{C8C16}	281.4	278.2	273.0	286.8	283.0
$r_{\text{H(Me)C5}}$	248.9 ^[c]	247.6	243.3	257.7	253.7
α	15.0	15.1	14.3	16.4	15.9
β	0.3	1.0	1.6	0.4	0.7
MD		0.7	2.3	-2.5	-1.5
MAD		0.9	2.5	2.7	1.7

[a] X-ray data (average of symmetry equivalent parameters) taken from reference [51]. [b] TZV(2df,2p) AO basis set. [c] Experimental C–H(Me) bond length adjusted to the SCS-MP2 value.

er, the deformation angle β (see Scheme 1) that describes the pyramidalization at C8/C16 is close to zero. This shows that the boat-type deformation of the ring (deformation angle α) is sufficient to place the methyl group in an optimal position. The shortest H(Me)...C(ring) distance in **3** is about 248 pm, which is 40 pm shorter than the corresponding optimum value of the benzene–methane van der Waals complex (MP2/TZV(2df,2p) value). The origin of the closer H...ring contact in **3** compared to an unstrained reference system is not clear at present, although it should be kept in mind that the ring deformations and bridges in general introduce non-negligible perturbations of the properties of benzene rings in cyclophanes.

The results from the SCS-MP2 treatment are again in good agreement with the experimental data (see Table 3). The mean absolute deviation (MAD) for all distances is only 0.9 pm and the largest error occurs for the IRD C8–C16 (3.2 pm too short). The important deformation angle α is almost exactly the same as experimental value. The standard MP2 treatment provides significantly less-accurate structural parameters. The single bonds are slightly too short and the IRD are too small by 8.4 and 5.6 pm, respectively. Both DFT treatments yield deviations in the opposite direction, as indicated by the negative mean deviation (MD). The bridging bond lengths are too long by 1.2 pm and for the inter-ring distances systematic overestimations are observed that reach 5 pm with B3LYP. Opposite to the common view (but similar as for **1** and **2**), the pure PBE

functional yields a more accurate structure than B3LYP, especially with respect to the transannular interactions. The overall accuracy of the three methods is $\text{SCS-MP2} \gg \text{DFT-PBE} > \text{MP2} \approx \text{DFT-B3LYP}$.

16-Methyl[2.2]metaparacyclophane: Metaparacyclophanes simultaneously contain structural features of meta- and paracyclophanes, that is, the *para*-substituted ring mainly shows a boat-shape deformation at the substituted sides, while the *meta*-substituted ring deforms mainly between the bridges (see Figure 1). The methyl group in **4** lies almost on top of the CC bond of the other ring thus introducing additional non-bonded interactions of C–H $\cdots\pi$ type as in **3**. Both, experimental and theoretical data show that the investigated compound has the second shortest IRD (between C3 and C14) of all phanes investigated. The deformation angles α and β are similar to the corresponding values in **1** and **3**, respectively. Inspection of Table 4 shows that the results from

Table 4. Comparison of experimental^[a] and calculated^[b] structural parameters of 16-methyl[2.2]metaparacyclophane (**4**). Distances r are given in pm, the deformation angles α_1 , β_1 , (*para*-substituted ring) and α_2 , β_2 (*meta*-substituted ring, methyl side) in degrees. The mean deviation [$\text{MD} = 1/N \sum r(\text{exptl}) - r(\text{calcd})$] and mean absolute deviation [$\text{MAD} = 1/N \sum |r(\text{exptl}) - r(\text{calcd})|$] are given for all distances.

	Method				
	Exptl	SCS-MP2	MP2	DFT-B3LYP	DFT-PBE
r_{C1C2}	158.9	157.5	157.2	158.7	158.6
r_{C2C3}	151.4	150.6	150.0	150.9	150.7
r_{C1C15}	153.2	151.6	151.1	152.0	152.0
r_{C3C4}	138.0	139.8	139.8	139.5	140.2
r_{C3C8}	138.1	140.0	140.0	139.7	140.4
r_{C4C5}	138.9	139.7	139.6	139.2	139.8
r_{C7C8}	140.2	139.0	139.0	138.6	139.2
r_{C14C15}	138.2	139.9	139.9	139.6	140.2
r_{C13C14}	139.0	139.3	139.2	138.8	139.5
r_{C15C16}	141.5	141.3	141.2	141.2	141.8
r_{C3C15}	277.3	274.3	271.0	283.0	280.7
r_{C7C12}	312.6	312.1	306.2	327.3	322.8
r_{C4C16}	318.1	316.2	312.7	325.8	324.5
α_1	12.1	12.7	12.1	14.3	14.1
β_1	14.9	15.0	15.1	14.7	14.6
α_2	10.3	12.3	11.6	14.0	13.5
β_2	1.7	2.5	2.8	1.3	1.5
MD		0.2	1.4	-2.3	-2.0
MAD		1.4	2.5	2.9	2.5

[a] X-ray data (average of symmetry equivalent parameters) taken from reference [46]. [b] TZV(2df,2p) AO basis set.

the SCS-MP2 treatment are not in perfect agreement with the experimental data. The MAD is larger (1.4 pm), α_2 deviates by more than two degrees, and some CC bond lengths are in error by almost 2 pm. A closer look at the experimental data^[45] reveals that these differences almost certainly result from experimental problems, probably disorder in the crystal. The structure determination is of relative poor quality as indicated by the accuracy of lattice constants, the standard deviation of bond lengths (0.6–1 pm), and the R value.^[45] Furthermore, some symmetry equivalent CC distances in the experimental structure deviate by 1–2 pm from each other. Nevertheless, the data seem to be accurate

enough to draw some conclusions about the performance of the methods applied. Again, SCS-MP2 is most accurate followed by MP2 and the two DFT methods. Especially the errors for the IRD with B3LYP are extremely large, reaching 15 pm for the distance C7–C12. Also the errors for the RDA α are larger, in the range 2–4°. This somewhat unsystematic behaviour, especially of B3LYP, is quite disappointing, because relative to compounds **1–3** no additional or new structural features are present in the metaparacyclophane.

2,6,15-Trithia[3^{4,10}][7]metacyclophane: Up to here, only hydrocarbons with two aromatic units have been considered. In order to put the conclusions on a more solid basis, a quite different cyclophane with one ring, three bridges, and heteroatoms (sulfur) is finally investigated. The compound 2,6,15-trithia[3^{4,10}][7]metacyclophane (**5**; Figure 1) has already been used by Pascal^[11] in a benchmark study of molecular structures with different quantum chemical methods. An additional feature of **5** is the close contact of the C–H bond pointing exactly into the middle of the benzene ring; this resembles the T-shaped structure of the benzene dimer. The experimental data are taken from reference [46]. Although structurally very different from the other phanes, the new SCS-MP2 approach also performs very well here (Table 5). This is indicated by a small overall MAD of

Table 5. Comparison of experimental^[a] and calculated^[b] structural parameters of 2,6,15-trithia[3^{4,10}][7]metacyclophane (**5**). Distances r are given in pm, the deformation angles α and β in degrees. The mean deviation [$\text{MD} = 1/N \sum r(\text{exptl}) - r(\text{calcd})$] and mean absolute deviation [$\text{MAD} = 1/N \sum |r(\text{exptl}) - r(\text{calcd})|$] are given for all distances.

	Method				
	Exptl	SCS-MP2	MP2	DFT-B3LYP	DFT-PBE
r_{C1S}	184.8	185.3	184.7	187.4	187.1
r_{CS}	183.1	183.8	183.2	185.4	185.0
r_{C7CS}	149.6	150.2	149.8	150.2	150.3
r_{C3C4}	152.0	153.5	153.0	154.1	154.0
r_{CS^9}	138.1	139.1	139.2	138.8	139.5
r_{C4CS}	309.8	307.7	305.0	314.5	313.0
r_{C4C9}	312.0	310.8	307.8	318.2	316.6
$r_{\text{H(C4)C9}}$	221.3 ^[c]	220.8	218.1	227.3	225.0
α	4.4	4.9	4.5	5.7	5.5
β	19.8	18.9	19.1	18.2	18.4
MD		-0.1	1.2	-3.1	-2.5
MAD		1.0	1.8	3.1	2.5

[a] X-ray data (average of symmetry equivalent parameters) taken from reference [46]. [b] TZV(2df,2p) AO basis set. [c] Experimental C–H bond length adjusted to the SCS-MP2 value.

1.0 pm and accurate nonbonded distances (errors of about 1–2 pm). The C–S bond lengths are described very accurately, although standard MP2 seems to perform slightly better for these parameters. Although only one ring is present in **5** and the nonbonded interactions occur between the π system and the saturated parts of the molecule, the errors from MP2 and DFT are similar to those of the other phanes. The nonbonded distances are about 3–5 pm too small by MP2 and too large by 5–6 pm (B3LYP) or 4–5 pm (PBE) with DFT. Larger errors of DFT are furthermore observed for the C–S bond lengths, which are too long by 2–3 pm. The

overall accuracy of the three methods is SCS-MP2 > MP2 > DFT-PBE > DFT-B3LYP.

Discussion

What is the reason for the DFT errors that are outside the usual error range for the prediction of organic structures? Although it is well known that common density functionals can not predict dispersive interactions,^[10] this argument is not fully satisfactory, because the IRD in cyclophanes are significantly below, for example, the VDW distance between graphite sheets (about 340 pm) and thus, the π orbitals (or equivalently, the electron densities) of the rings begin to overlap. This is clearly seen in iso-surface plots of the HOMO and LUMO of **1** given in Figure 2.

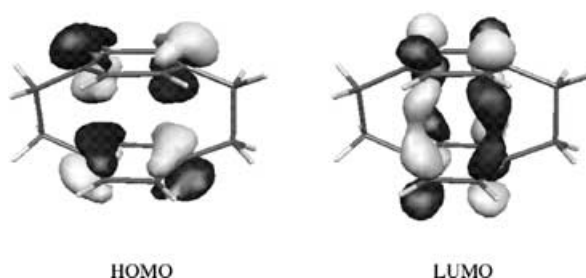


Figure 2. Iso-surface plots of the frontier orbitals of [2.2]paracyclophane at the HF/cc-pVDZ level. Plots with various other types of basis sets or when using Kohn–Sham (DFT) orbitals look qualitatively similar.

While the HOMO has a nodal surface between the two rings (antibonding), the opposite is observed for the LUMO, which shows considerable bonding character in the inter-ring region (other π and π^* orbitals not shown also display this behavior). In the MP2 treatments, HOMO–LUMO double excitations de-populate the antibonding and populate the bonding orbital to some extent and thus reduce the steric (Pauli) repulsion of the fragments. This effect is overestimated by standard MP2 and corrected with the SCS scheme. On the other hand, mean-field approaches like Hartree–Fock or Kohn–Sham DFT do not “know” about the bonding character of the LUMO (because it is unoccupied in the ground state) and thus yield less attraction (too much repulsion). In summary, the situation in cyclophanes can be best described by strong π – π electron correlations between the two rings. It should be distinguished from “normal” VDW interactions because of the overlapping densities of the fragments and may be termed as “overlap-dispersive” interactions. Note that this classification is also in line with the negligible effect of diffuse basis functions on the geometry of **1** (vide supra) which would be much stronger in the pure VDW case.

Figure 3 shows the potential-energy curves (aug-cc-pVTZ AO basis) for the face-to-face (D_{6h}) dimerization of benzene as an attempt to quantify the conclusion presented above. The inset shows the difference with respect to the SCS-MP2 interaction energy, which is taken as a reference because SCS-MP2 provides IRD close to experiment and, thus, the

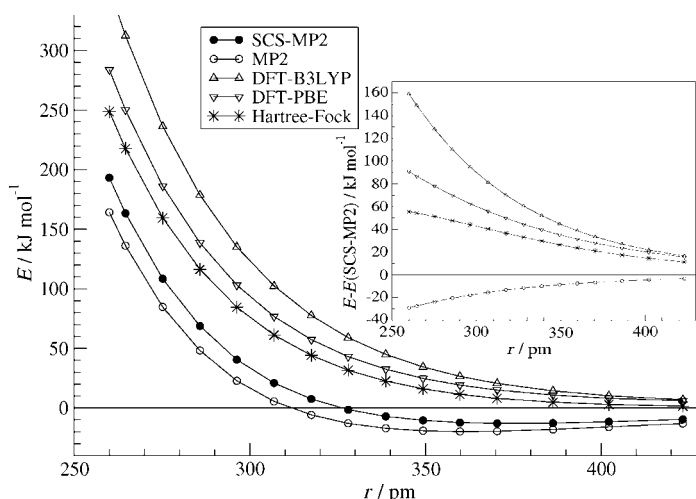


Figure 3. Potential-energy curves (aug-cc-pVTZ AO basis) for the face-to-face (D_{6h}) dimerization of benzene (r is the inter-ring distance). The benzene fragments are not optimized and kept fixed at the benzene equilibrium geometry (DFT-B3LYP/TZV(d,p)). The inset shows the difference with respect to the SCS-MP2 interaction energy taken as reference.

interaction potential should be most reliable. Note, that the data are not corrected for basis set superposition error, because this is in principle impossible for the “real” situation of the phanes. While MP2 and SCS-MP2 yield potential-energy curves with very broad minima between 330 and 420 pm (with D_e values of -20 and -13 kJ mol⁻¹, respectively), both density functionals as well as Hartree–Fock (HF) yield purely repulsive potentials. The deviation with respect to the SCS-MP2 reference increases in the case of HF and DFT and decreases for MP2 as the two benzene molecules approach each other. At about 300 pm distance, which is considered as typical for the phanes considered,^[47] the errors are -18 , 94 and 63 kJ mol⁻¹ for the MP2, DFT-B3LYP and DFT-PBE interactions, respectively. These values are qualitatively in line with the results for the computed IRD which show the same trend, that is, MP2 < SCS-MP2 < DFT-PBE < DFT-B3LYP. Somewhat surprisingly, however, the HF errors are smaller compared to both density functionals, but this is actually not reflected in the geometries of cyclophanes.^[48]

Conclusions

Correlated ab initio quantum chemical methods based on second-order perturbation theory (MP2, SCS-MP2) and density functional theory (DFT) have been used to calculate the structures of five typical cyclophanes with one and two aromatic rings. For accurate experimental structures (i.e., **1–3** and **5**), the new SCS-MP2 model provides mean absolute deviations for bonded and nonbonded CC distances below 1 pm. The nonbonded inter-ring distances are accurate to about 1–2 pm, and the errors for the characteristic benzene ring deformation angles α and β are less than about 1°. It can thus be concluded that theory has reached a quantitative description of cyclophane structures that is competitive to experimental structure determinations. Larger differences

between SCS-MP2 and experimental data found for the metaparacyclophane are indicative of experimental errors or of a slightly disordered crystal structure. The standard MP2 method accurately predicts (as SCS-MP2) CC bond lengths, but fails for the description of the nonbonded inter-ring distances. Dispersive-type electron correlation effects, which are in general overestimated by MP2, are responsible for this. This results in too short nonbonded contacts and slightly less-accurate deformation angles. The two density functionals B3LYP and PBE show the opposite behavior. Due to the missing effect of double excitations between occupied inter-ring antibonding and unoccupied inter-ring bonding orbitals, the nonbonded distances are overestimated at the DFT level. The effect is more pronounced for the B3LYP than for the pure PBE functional, which can already be observed in model calculations for the face-to-face oriented benzene dimer. These findings are also in line with previous studies showing that PBE provides in some cases a qualitative correct picture of weak van der Waals type interactions^[49]. The DFT-PBE method is thus recommended for initial molecular modeling of such structures; however, they should be accompanied by SCS-MP2 treatments employing large AO basis sets in order to obtain conclusive predictions.

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft in the framework of the SFB 424 (“Molekulare Orientierung als Funktionskriterium in chemischen Systemen”).

- [1] P. M. Keehn, S. M. Rosenfeld, *Cyclophanes*, Academic Press, New York, **1983**.
- [2] F. Vögtle, *Cyclophane Chemistry*, Wiley, New York, **1993**.
- [3] *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim (Germany), **2004**.
- [4] M. Suzuki, N. Amano, J. Kakinuma, M. Tateno, *J. Mol. Biol.* **1997**, *274*, 421.
- [5] D. H. Mathews, J. Sabina, M. Zuker, D. H. Turner, *J. Mol. Biol.* **1999**, *288*, 911.
- [6] S. Bommarito, N. Peyret, J. SantaLucia, *Nucleic Acids Res.* **2000**, *28*, 1929.
- [7] T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley, New York, **2000**.
- [8] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**.
- [9] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim (Germany), **2001**.
- [10] M. Allen, D. J. Tozer, *J. Chem. Phys.* **2002**, *117*, 11113.
- [11] R. A. Pasacal, *J. Phys. Chem. A* **2001**, *105*, 9040.
- [12] M. Habel, C. Niederalt, S. Grimme, M. Nieger, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1471.
- [13] S. Grimme, W. Mennicke, F. Vögtle, M. Nieger, *J. Chem. Soc. Perkin. Trans. 2*, **1999**, 521.
- [14] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
- [15] D. Cremer, in *Encyclopedia of Computational Chemistry, Vol 3* (Ed.: P. von R. Schleyer), Wiley, New York, **1998**.
- [16] S. Tsuzuki, K. Honda, T. Uchimura, M. Mikami, *J. Chem. Phys.* **2004**, *120*, 647.
- [17] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095.
- [18] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [19] P. J. Stevens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [20] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [21] TURBOMOLE (Vers. 5.6): R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss. Universität Karlsruhe **2003**; see also: <http://www.turbomole.com>.
- [22] E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41.
- [23] J. L. Whitten, *J. Chem. Phys.* **1973**, *58*, 4496.
- [24] B. I. Dunlap, W. D. Connolly, J. R. Sabin, *J. Chem. Phys.* **1979**, *71*, 3396.
- [25] O. Vahtras, J. Almlöf, M. W. Feyereisen, *Chem. Phys. Lett.* **1993**, *213*, 514.
- [26] F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331.
- [27] D. E. Bernholdt, R. J. Harrison, *Chem. Phys. Lett.* **1996**, *250*, 477.
- [28] The basis sets are available from the TURBOMOLE homepage <http://www.turbomole.com> via the FTP Server Button (in the subdirectories basen, jbasen, and cbasen).
- [29] F. Weigend, A. Köhn, C. Hättig, *J. Chem. Phys.* **2001**, *116*, 3175.
- [30] S. Grimme, *J. Comput. Chem.* **2003**, *24*, 1529.
- [31] M. Piacenza, S. Grimme, *J. Comput. Chem.* **2004**, *25*, 83–99.
- [32] F. Goumans, A. W. Ehlers, K. Lammertsma, E.-U. Würthwein, S. Grimme, unpublished results.
- [33] I. Hyla-Krispin, M. Schlosser, S. Grimme, unpublished results.
- [34] M. Gerenkamp, S. Grimme, *Chem. Phys. Lett.*, in press.
- [35] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.
- [36] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.
- [37] R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [38] F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380.
- [39] The X-ray crystal structure of [2.2]paracyclophane was recently reinvestigated with higher precision at low temperature (19 K): D. Stalke, Universität Würzburg, unpublished results. The author is grateful to Prof. Stalke for disclosing to us the atomic coordinates of **1**, enabling us to obtain more conclusive comparisons with the theoretical data.
- [40] C. J. Brown, *J. Chem. Soc.* **1953**, 3265.
- [41] H. Hope, J. Bernstein, K. N. Trueblood, *Acta Crystallogr.* **1972**, *28*, 1733.
- [42] S. E. Walden, D. T. Glatzhofer, *J. Phys. Chem. A* **1997**, *101*: 8233.
- [43] D. Henseler, G. Hohlneicher, *J. Phys. Chem. A* **1998**, *102*, 10828.
- [44] M. O. Sinnokrot, W. F. Valeev, C. D. Sherrill, *J. Am. Chem. Soc.* **2002**, *124*, 10887.
- [45] T. Yamato, J. Matsumoto, K. Tokuhisa, K. Tsuji, K. Suehiro, M. Tashiro, *J. Chem. Soc. Perkin Trans. 1* **1992**, 2675.
- [46] R. A. Pascal, C. G. Winans, D. Van Engen, *J. Am. Chem. Soc.* **1989**, *111*, 3007.
- [47] The face-to-face structure of the benzene dimer cannot directly be compared with the situation of the cyclophanes, because owing to the ring deformation there may be several different IRD. These deformations furthermore shift electron density from the “interior” of a phane to the outer sides; this reduces steric repulsion. The interaction energies at particular distances in Figure 3 are thus not directly transferable to strain components in cyclophanes.
- [48] The HF geometry of **1**, for example, is very similar to that from DFT-B3LYP, that is, with D_{6h} symmetry and the IRD are within 1 pm of the corresponding B3LYP values. The reason for this is probably a compensation of the overestimated π - π interactions by correlation effects in the σ system which are absent in HF.
- [49] I. Hyla-Krispin, S. Grimme, G. Haufe, *Chem. Eur. J.*, **2004**, in press.
- [50] A. W. Hanson, T. S. Cameron, *J. Chem. Res.* **1980**, 4201.
- [51] A. W. Hanson, *Acta Crystallogr.* **1962**, *15*, 956, .

Received: January 29, 2004

Published online: May 18, 2004