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Structure and NMR Spectra of Some [2.2]Paracyclophanes. The Dilemma of [2.2]Paracyclophane Symmetry

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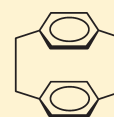
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S Supporting Information

ABSTRACT: Density functional theory (DFT) quantum chemical calculations of the structure and NMR parameters for highly strained hydrocarbon [2.2]paracyclophane **1** and its three derivatives are presented. The calculated NMR parameters are compared with the experimental ones. By least-squares fitting of the ¹H spectra, almost all *J*_{HH} coupling constants could be obtained with high accuracy. Theoretical vicinal *J*_{HH} couplings in the aliphatic bridges, calculated using different basis sets (6-311G(d,p), and Huz-IV) reproduce the experimental values with essentially the same root-mean-square (rms) error of about 1.3 Hz, regardless of the basis set used.

These discrepancies could be in part due to a considerable impact of rovibrational effects on the observed *J*_{HH} couplings, since the latter show a measurable dependence on temperature. Because of the lasting literature controversies concerning the symmetry of parent compound **1**, *D*_{2h} versus *D*₂, a critical analysis of the relevant literature data is carried out. The symmetry issue is prone to confusion because, according to some literature claims, the two hypothetical enantiomeric *D*₂ structures of **1** could be separated by a very low energy barrier that would explain the occurrence of rovibrational effects on the observed vicinal *J*_{HH} couplings. However, the *D*_{2h} symmetry of **1** with a flat energy minimum could also account for these effects.



*D*₂ or *D*_{2h} structure?

INTRODUCTION

Highly strained cyclophanes with small bridges are characterized by a distorted structure compared to unstrained hydrocarbons.^{1–3} These distortions are known to influence, among others, NMR parameters which can be regarded as a very sensitive measure of molecular structure.^{4,5} Therefore, a combined theoretical and experimental study of chemical shifts and coupling constants has been undertaken for [2.2]paracyclophane **1** and its three derivatives **2–4**. (Please note that the atom numbering in the structures shown in the formulas is different from the one adopted by the International Union of Pure and Applied Chemistry (IUPAC). It was developed to allow us to compare results within the series.) X-ray structures of **1**, **2**, and **4** have been reported.^{6–10} However, as will be discussed below, there has been a vivid discussion of whether the parent [2.2]paracyclophane **1** has an eclipsed *D*_{2h} or twisted *D*₂ equilibrium geometry, where in the latter the mutual twist of the benzene rings is combined with a twist around the C13C14 and C15C16 bridges in spite of the fact that the published experimental X-ray data⁸ measured at 100 K, where no disorder occurs, unequivocally favor the former structure. On the other hand, an analysis of IR spectra lead Walden and Glatzhofer¹¹ to conclude that a small twist (characterized by a *C*_{sp2}*C*_{sp3}*C*_{sp3}*C*_{sp2} torsional angle of 3.9°) is present, whereas unpublished X-ray

results by Stalke measured at 19 K yielded a twist larger than 10°¹² for another crystalline phase than that present at room temperature.⁴⁸

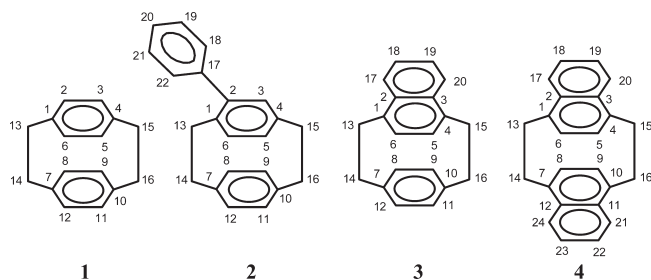
From most of these studies and from the data collected in the Cambridge Structural Database (CSD),^{13,14} the main conclusions for cyclophanes with multiple ethylene bridges *C*_{sp2}*C*_{sp3}*C*_{sp3}*C*_{sp2} are that (i) there is considerable disorder at room temperature in the observed structures and (ii) the *C*_{sp2}*C*_{sp3}*C*_{sp3}*C*_{sp2} torsional angles are mostly less than or equal to 3°.^{6,15,16} Interestingly, for superphane **5**, with six bridges, it is close to zero.¹⁷ However, for [2.2]paracyclophane **1** the structure published by Lyssenko et al.⁸ measured at 100 K exhibits no disorder and has *D*_{2h} symmetry. It should be stressed that a comparison of experimental and computed geometries is often very difficult since the latter refers to isolated molecules while the former is usually measured in the solid state.

The structural distortions in [2.2]paracyclophane **1** and their influence on the spectra are of fundamental importance. Unfortunately, theoretical studies of **1** are equivocal, and to the best of our knowledge, they have not been reviewed.

Received: June 17, 2011

Revised: August 16, 2011

Published: August 17, 2011



In addition, no calculations on 2–4 have been reported. The computations on **1** dealt with structural distortions,^{8,11,18–20} a ring current in the molecule,²¹ through-bond, through-space,^{8,22} and transannular interactions,⁸ normal vibrations,^{11,22} and the importance of electron correlation effects for the π – π interactions in cyclophanes¹⁹ using both ab initio and density functional theory (DFT) methods. Kama and Muchall carried out DFT calculations for 10 substituted [2.2]paracyclophanes and three [3.3]paracyclophanes and analyzed their geometries and electronic structures.²³ On the basis of such model calculations they claim that the (TD-)PBE0/6-31+G(d,p) approach is appropriate for the description of π -stacking interactions in constrained systems such as the base pairs in oligonucleotides.

As already mentioned, experimental results⁸ concerning the mutual twist of the benzene rings in **1** have been often neglected in theoretical studies. On the basis of self-consistent field (SCF) (STO-3G) calculations, Canuto and Zerner²⁴ analyzed the interring separation of the lowest excited and ionized states of [2.2]paracyclophane. Shen and co-authors²⁵ studied fluorescence excitation spectra of [2.2]paracyclophane in supersonic jets and carried out calculations allowing them to explain the extensive vibronic structure in the lowest-lying electronic transition. Walden and Glanzhofer¹¹ calculated the structure and normal vibrations of **1** using the hybrid Hartree–Fock/gradient-corrected DFT B3LYP/4-21G(d) method and obtained a twist angle ϕ of 3.9°, in good agreement with the value of 3.2° reported by Hope et al., although the angle was poorly defined in the latter work.⁷ However, the energy difference between the minima and the corresponding D_{2h} saddle point in the Walden and Glanzhofer work corresponding to 1 cal/mol barrier is certainly within the limits of error. Henseler and Hohlneicher,¹⁸ using MP2 (6-31G(d)), obtained ϕ equal to 21.8°. They incorrectly stated in the paper by Hope and co-workers that the value of the torsional angle has not been reported even though the value of 3.2° could be extracted from the data given in that work. In a combined experimental and computational (HF, MP2, B3LYP with 6-31G(d) basis set) study, Lyssenko et al.⁸ found the eclipsed structure ($\phi = 0^\circ$) as the minimum structure with a considerable anisotropy of twist vibrations even at 100 K. Their argument in favor of the low force constant for the twist on the basis of an inspection of the CSD data on the derivatives of [2.2]paracyclophane does not seem valid since a substitution on either aromatic ring or on the bridge introduces steric strain that would force a twist. The claim by Lyssenko et al.⁸ that there are no through-space interactions between the rings in **1** also seems questionable.

On the basis of B3LYP/6-31G** calculations of the structure of **1**, Pelloni and co-workers²¹ obtained a slightly twisted structure, but they carried out the calculations of magnetic properties for the ideal D_{2h} structure since they found the results to be independent of such a simplifying assumption. According to the most reliable calculations reported by Grimme,¹⁹ the

lowest energy structure is of D_2 symmetry, where the barrier to the interconversion between the two (equivalent) twisted isomers calculated at the SCS-MP2/cc-pVTZ level is as low as 0.2 kcal/mol. In the paper by Grimme there was no discussion of the experimental findings by the Lyssenko group.⁸ Instead, Grimme compared his results with those of Stalke measured at 19 K (where the value of 12.6° for the twist angle was found),¹² a result that has never been published. Grimme's¹⁹ study demonstrated that the ϕ value is dependent on the method applied. Except for the DFT-B3LYP result yielding a zero twist angle,⁸ all other values were larger than 10° (17.6°, 18.7°, and 10.7° using SCS-MP2, MP2, and DFT-PBE, respectively). Caramori and co-workers²⁰ also found that “the dihedral angles of the ethano bridges are very dependent on the model”. Their geometry optimizations using the cc-pVDZ basis set for all methods, as well as MP2/6-31G(d;0.25) calculations, have yielded twisted D_2 structures, while B3LYP have resulted in a close to the eclipsed D_{2h} conformer. Recently, Bachrach²⁶ reported DFT calculations for [2.2]-, [3.3]-, and [4.4]paracyclophanes using B3LYP, M06-2x, B97-D, and ω B97X-D functionals and compared the results with the literature values for some other functionals, with the aim of finding which one describes the geometry, in particular the twist of the C1C13C14C7 angle, the best. Unfortunately, Bachrach does not give the value of 3.2° as the experimental value reported by Hope et al.,⁷ but rather a much larger angle of 12.6°. As the second experimental result, Bachrach cites the unpublished data by Stalke at 19 K,¹² also dismissing the Lyssenko et al. X-ray analysis.⁸ Interestingly, only one of the functionals studied or cited by Bachrach gives a value for the $C_{sp^2}C_{sp^3}C_{sp^3}C_{sp^2}$ torsional angle of ca. 10°, some of them yielding values as large as 18°.

Despite the many studies advocating a large twist angle, we believe that the zero value of the angle determined by the Lyssenko group or the small values less than 5° are the most reliable. The very low energy differences of 0.2 kcal/mol between the D_{2h} and the D_2 structures calculated by Grimme¹⁹ at the SCS-MP2/cc-pVTZ level and that of 1 cal/mol reported by Walden and Glanzhofer¹¹ on the basis of DFT calculations using a small 4-31G(d) basis set indicate that an experimental solution to the problem is not trivial.

With respect to NMR spectra of cyclophanes, three comprehensive reports by Ernst^{4,5,27} have to be mentioned. The spectra of **1**,²⁸ **2**,²⁹ **3**,³ and **4**³⁰ have been reported. The proton and carbon chemical shifts in **1** were calculated by Caramori et al.²⁰ while Bifulco and Mangoni³¹ analyzed 1H – 1H scalar coupling across the two stacked aromatic rings in a [2.2]paracyclophane derivative. Some NMR data were given in synthetic works, although the data on the coupling constants are scarce in these cases. Therefore, repeating the measurements of the NMR spectra for **1**–**4** is of interest, with a focus on the vicinal J_{HH} couplings within the aliphatic bridges and the possible temperature dependences of the former, as this could provide further insight into the character of the energy minima of these compounds in solution.

EXPERIMENTAL SECTION

Reagents. [2.2]Paracyclophane **1** of 99% purity was purchased from Alfa Aesar. The syntheses of **2**,⁹ **3**,³² and **4**³² have been reported earlier.

NMR Measurements. All room temperature NMR experiments were performed in $CDCl_3$ solutions on a Bruker DRX-500 spectrometer using the XWIN NMR acquisition and processing

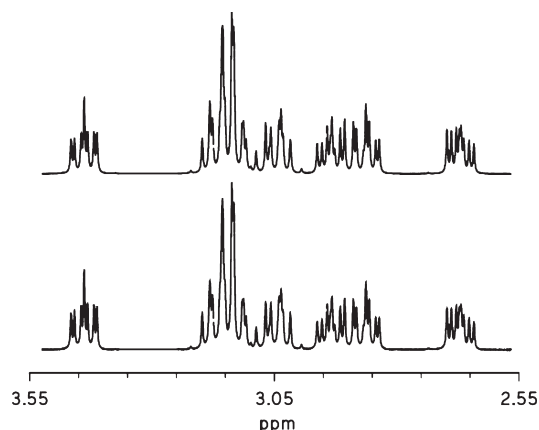


Figure 1. Partial experimental ^1H NMR spectrum (500 MHz) at room temperature of the aliphatic protons in **2** (bottom) and the theoretical best fit spectrum (top).

program. The 5 mm triple broadband inverse probe equipped with a z -gradient coil was used for ^1H and ^{13}C measurements. All ^{13}C , ^1H , and 2D correlation experiments were carried out using the inverse gradient technique. Signal assignments for **2**, **3**, and **4** were carried out by means of 1D nuclear Overhauser effect (NOE), correlation spectroscopy (COSY), and (^{13}C , ^1H)-HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation) experiments. Variable-temperature ^1H spectra were recorded on a Bruker 300 Avance II spectrometer equipped with a broadband inverse probehead and a BVT 3200 temperature control unit. The reported temperatures were read from the display of the temperature unit.

The values of absolute shieldings and chemical shifts are given in parts per million (ppm) and those of coupling constants in hertz (Hz).

Analysis of NMR Spectra. ^{13}C chemical shifts and proton–carbon and carbon–carbon coupling constants were read from spectra. The ^1H NMR spectra of **2–4** contain nonfirst-order patterns; the same holds for the ^{13}C satellites of the aliphatic protons' singlet in **1**. Thus, to determine the exact values of the proton chemical shifts and proton–proton coupling constants, the spectra were analyzed numerically using an in-house FORTRAN program. It performs iterative least-squares fits to the experimental line shapes. A typical fit outcome is shown in Figure 1 for the aliphatic protons in **2**.

Computational Details. The quantum chemical calculations were performed using either Gaussian³³ (at the University of Tromsø and at ICM at Warsaw University) or the Dalton quantum chemistry program (Dalton, an ab initio electronic structure program, Release 2.0, 2005, at the University of Tromsø; see <http://www.kjemi.uio.no/software/dalton/dalton.html>). The Dalton calculations were performed in parallel using 90 processors on the local supercomputer cluster installed at the University of Tromsø and 32 processors at the ICM, University of Warsaw.

The molecules were optimized using Becke's three-parameter hybrid exchange functional³⁴ and the Lee–Yang–Parr correlation functional,³⁵ commonly referred to as B3LYP.³⁶ The correlation-consistent polarized valence double- ζ and triple- ζ basis sets of Dunning,³⁷ 6-311G(d,p)³⁸ and Huz-IV^{39,40} basis sets were used for the geometry optimization, using the first-order geometry optimization methods of Bakken and Helgaker.⁴¹ The

calculations of the shielding constants and spin–spin couplings constants were done applying the B3LYP functional, using the implementations of shielding constants^{39,40} and indirect spin–spin coupling constants^{42,43} employing the 6-311G(d,p) and Huzinaga-IV basis sets. The latter basis set was suggested by Schindler and Kutzelnigg⁴³ based on the atomic basis sets of Huzinaga.⁴⁴ London atomic orbitals⁴⁵ were used to ensure gauge origin independence of the calculated shielding constants.⁴⁶

Some values of bond lengths and angles in the tables can be slightly different from those in original papers since they were measured from cif files taken from CSD.¹³ This approach was adopted since the original papers do not always contain all of the necessary data.

RESULTS AND DISCUSSION

Geometry. A collection of geometrical parameters for the whole series calculated at the B3LYP/cc-pVTZ level is presented in Table SUP-1 in the Supporting Information. As discussed in the Introduction, the published results for the parent compound **1** exhibit considerable differences. Therefore, our own data for this important molecule, obtained with various basis sets (Table 1), will be discussed in detail first, together with the corresponding experimental values from the most reliable determinations.

[2.2]Paracyclophane 1. As discussed in the Introduction, the symmetry of [2.2]paracyclophane **1** is still debated in spite of its unequivocal determination. Understandably, in view of the low barrier to internal rotation around the $\text{C}_{\text{sp}3}\text{C}_{\text{sp}3}$ bond in this compound the room-temperature experimental X-ray results exhibit disorder and depend significantly on temperature. For instance, the $\text{C}_{\text{sp}3}\text{C}_{\text{sp}3}$ bridge bond lengths of 1.558 and 1.630 Å determined in the Lonsdale group at 93 and 295 K, respectively, differ by more than 0.07 Å.⁶ Smaller, but also significant, differences occur for the $\text{C}_{\text{sp}2}\text{C}_{\text{sp}3}$ and $\text{C}_{\text{sp}2}(\text{H})\text{C}_{\text{sp}2}(\text{H})$ bonds. On the other hand, rather unexpectedly, in the same paper the $\text{C}_{\text{sp}2}\text{C}_{\text{sp}3}$ bond was found to be longer at 90 K than at 295 K. Moreover, the bond lengths measured at the same (or close) temperatures, differ considerably; for example, the $\text{C}_{\text{sp}2}\text{C}_{\text{sp}2}$ bridge bond length was found to be longer than 1.558⁶ at 93 K, 1.579 at 100 K,⁸ and 1.630⁶ and 1.569⁷ at 297 K. The fundamental discrepancy concerning the symmetry of **1** is discussed in the Introduction. Our own theoretical results concerning this question are discussed below.

Torsional Angles. The calculated and experimental values of the C1C13C14C7 dihedral angle describing the mutual twist of the aromatic rings and those describing their nonplanarity are collected in Table 1. The calculated twist angles do not exceed 1.2°. If these results describe the real situation in solution, the D_{2h} symmetry can safely be assumed for **1**, in agreement with the determination made by the Lyssenko group.⁸

In view of the low barrier to twisting,^{8,19} a small value of the $\text{C}_{\text{sp}2}\text{C}_{\text{sp}3}\text{C}_{\text{sp}3}\text{C}_{\text{sp}2}$ angles cannot be excluded. However, taking into account that MP2 calculations are known to overestimate nonbonding repulsions (as shown, e.g., by the Grimme results),¹⁹ we believe that the $\text{C}_{\text{sp}2}\text{C}_{\text{sp}3}\text{C}_{\text{sp}3}\text{C}_{\text{sp}2}$ torsional angles should not be larger than ca. 5° and probably even smaller. It should be stressed that the large experimental value of Stalke¹² was only cited¹⁹ and still has not been published. Such a high experimental value of the angle has furthermore not been

Table 1. Torsional Angles, Bond Lengths, and Bond Angles in **1**, Calculated Using Different Functionals and the Corresponding Experimental Results

	B3LYP/ cc-pVDZ	B3LYP/ cc-pVTZ	KT1 ^{46–48} / cc-pVTZ	KT2 ^{46–48} / cc-pVTZ	B3LYP/Huz IV	exp. ⁷ eclipsed	exp. ⁸
Torsional Angles (in Degrees)							
C1C13C14C7	0.0	−0.4	1.1	1.2	−0.4	0.0	3.2
C2C3C4C5	14.9	15.2	13.5	13.6	15.2	14.4	12.6
Bonds (in Å)							
C13C14	1.612	1.612	1.617	1.597	1.611	1.579	1.591(1.569)
C1C13	1.515	1.510	1.511	1.494	1.509	1.508	1.511 (1.514)
C1C2	1.404	1.397	1.409	1.393	1.397	1.400	1.386 (1.394)
C2C3	1.397	1.389	1.402	1.387	1.389	1.392	1.387 (1.394)
Bond Angles (in Degrees)							
HC13H	106.8	106.9	107.7	107.6	106.9	109.0	nm ^a
C1C2C3	120.7	120.7	120.7	120.7	120.8	120.7	120.7
C1C13C14	113.6	113.7	112.7	112.7	113.7	113.6	113.7
C2C1C6	116.8	116.8	117.2	117.2	116.7	117.0	117.0
C2C1C13	121.0	120.9	120.8	120.8	121.0	120.9	120.8
C4C1C13	156.4	156.2	157.3	157.3	156.2	156.4	167.4

^a Not measured.

reported by any other group. This discrepancy can be due to the phase transition at 50 K mentioned earlier.⁴⁸ As discussed above, the recent calculations by Bachrach²⁶ using other functionals than B3LYP yielded much larger values for the C_{sp2}C_{sp3}C_{sp3}C_{sp2} torsional angle, in disagreement with all experimental observations except the unpublished experimental results.¹²

In contrast to the determination of the torsional angles describing the bridge twist, all computed values of the C2C3C4C5 angle describing the nonplanarity of the aromatic rings are very close, indicating that this deformation does not significantly depend on the bridge twisting. The computed values agree well with the experiment.

Bond Lengths. Most calculated bond lengths are larger than the corresponding experimental data, but the values computed using KT2 are closest to the results by Lyssenko group.⁸ The calculated C13C14 bond length, that is, C_{sp3}C_{sp3}, are too long, in particular as compared to the experimental results of the Lyssenko group.⁸ However, all of the results suggest a significant lengthening of the bond lengths, largely overestimated by all methods except the KT2/cc-pVTZ calculations. In agreement with these findings, this lengthening is much smaller for the C_{sp3}C_{sp2} bonds than for the C_{sp3}C_{sp3} bond. For all methods used, the C1C2 bond is calculated slightly longer than the C2C3 one. This trend agrees with the results of the Lyssenko group but not with those of Hope et al.⁸ The calculations using the KT2/cc-pVTZ functional underestimate the bond lengths. We note, however, that the KT2 functional has been developed primarily with the purpose of calculating magnetic properties and furthermore that vibrational effects because of this are partially accounted for in the parametrization of the functional.⁵⁷

Bond Angles. Except for the determination of the C4C1C13 bond angle by Hope et al.⁷ (which suggests a deviation of the Csp2Csp3 bond from the plane of the corresponding aromatic ring) and the X-ray determined (and thus quite inaccurate) HC13H bond angle value of Lyssenko et al.,⁷ there is a very

satisfactory agreement among all experimental and calculated values for the bond angles.

Phenyl[2.2]paracyclophane 2, Benzene[2.2]paracyclophane 3, and *trans*-[2.2]Naphthalenephane 4. As mentioned previously, an X-ray analysis of **2** has been published,⁹ but to our best knowledge, no calculations for this molecule have been reported. In view of the possibility of an internal rotation around the C2C17 bond in **2** in solution and in the gas phase (to which the calculations refer), there is a possibility of two rotational isomers with C1C2C17C18 and C3C2C17C18 torsional angles adopting values of ca. 48° and −134°. However, the calculated energy difference of 2.2 kcal/mol between these isomers corresponds to an approximately 98% prevalence of the former rotamer. Thus, only the data for this conformer will be compared to the experimental results. No experimental determination of the geometry of **3** could be found, only the structure of the complex with GaBr₄.⁵² As mentioned in the Introduction, there is only one experimental study of the *trans*-[2.2]naphthalenophane structure.¹⁰ However, the existence of two independent molecules in the unit cell makes a comparison of the experimental structural parameters with the calculated values difficult. The bond lengths and angles calculated using B3LYP/Huz-IV for cyclophanes **1–4** and the corresponding experimental values (for **1**, **2**, and **4**) are collected in Table SUP-1 of the Supporting Information.

The most unusual features of the structure of the [2.2]paracyclophanes under investigation are the lengthening of the C_{sp3}C_{sp3} bridge bonds and nonplanar distortions of the cyclophane aromatic rings. The calculated values for the inter-ring bridge bonds are too large, but they reproduce the observed lengthening of the bonds. The experimental (vs calculated by us) values of C13C14 and C15C16 bond lengths are 1.579³ and 1.591 Å⁴ (calcd 1.611 Å) for **1**, 1.548⁹ and 1.581 Å⁹ (calcd 1.608 and 1.605 Å) for **2**, (calcd 1.612 Å) for **3**, and 1.569 and 1.574 Å (calcd 1.599 Å) for **4**. For most saturated bridge bonds the lengthening is overestimated by about 0.03 Å by the calculations, although the excess reaches 0.06 Å for the bridge close to the

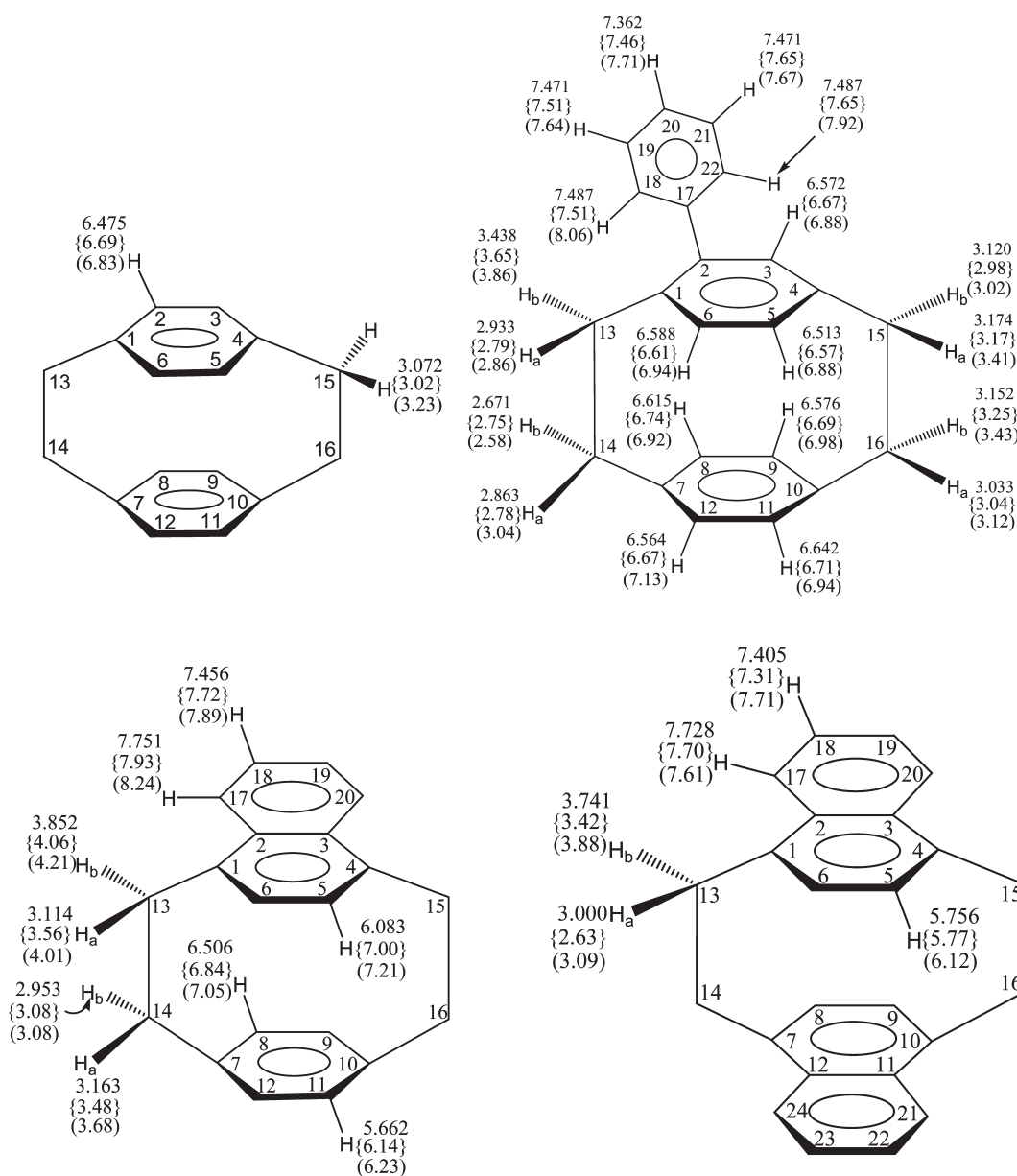


Figure 2. ^1H chemical shifts for **1** (upper left), **2** (upper right), **3** (lower left), and **4** (lower right); exp. values, no brackets; calcd using the B3LYP functional are denoted by curly brackets and parentheses for 6-311G(d,p) and Huz-IV basis sets, respectively. In *p*-xylene methyl protons absorb at 2.296 ppm, aromatic ones at 7.046 ppm, and carbon at 134.66, 128.97, and 20.90 ([http://en.wikipedia.org/wiki/P-Xylene_\(data_page\)](http://en.wikipedia.org/wiki/P-Xylene_(data_page)))).

phenyl substituent in **2**. The differences between the calculated and the experimental values of the $\text{C}_{\text{sp}^2}\text{C}_{\text{sp}^3}$ and $\text{C}_{\text{sp}^2}\text{C}_{\text{sp}^2}$ bond lengths are in most cases less than 0.01 Å. For molecules **1**, **2**, and **4**, nonplanar boat structures of the cyclophane aromatic rings have been found both experimentally and by our calculations. Similarly, the calculated structure of **3** suggests a boat structure. The rings are characterized by C1C2C3C4 torsional angles close to zero with a maximum value of 2.1° (calc) and 1.6° (exp) obtained, understandably, for the phenyl-substituted molecule **2**. The experimental values for the torsional angles are also reproduced satisfactorily by the calculations except for the angles C1C13C14C7 and C3C2C17C18 in phenyl-substituted [2.2]-paracyclophane **2**. It should be emphasized that the experimental value for the latter angle can depend considerably on the crystal forces, while the calculated angle was obtained for the isolated

molecule. All trends in the experimental values for the bond angles are reproduced very accurately by the calculations. In most cases the differences are smaller than 0.5° , and in very few cases they exceed 1° . The C2C1C6 , C3C4C5 , C8C7C12 , and C9C10C11 as well as the C18C17C22 and symmetrical ones in **3** and **4** angles are squeezed to the value of ca. 117° , whereas other angles in the cyclophane aromatic rings are slightly expanded. The considerable tilt of the substituents out of the corresponding aromatic cyclophane ring plane is well-reproduced by the calculations (the calculated value of 156.9° of the C1C4C15 angle while the corresponding experimental result of 157.9° is considerably larger than the ca. 120° expected for the planar structure). On the other hand, the small tilt of the phenyl substituent of **2** represented by the C2C17C20 and C5C2C17 angles is also satisfactorily reproduced by the calculations.

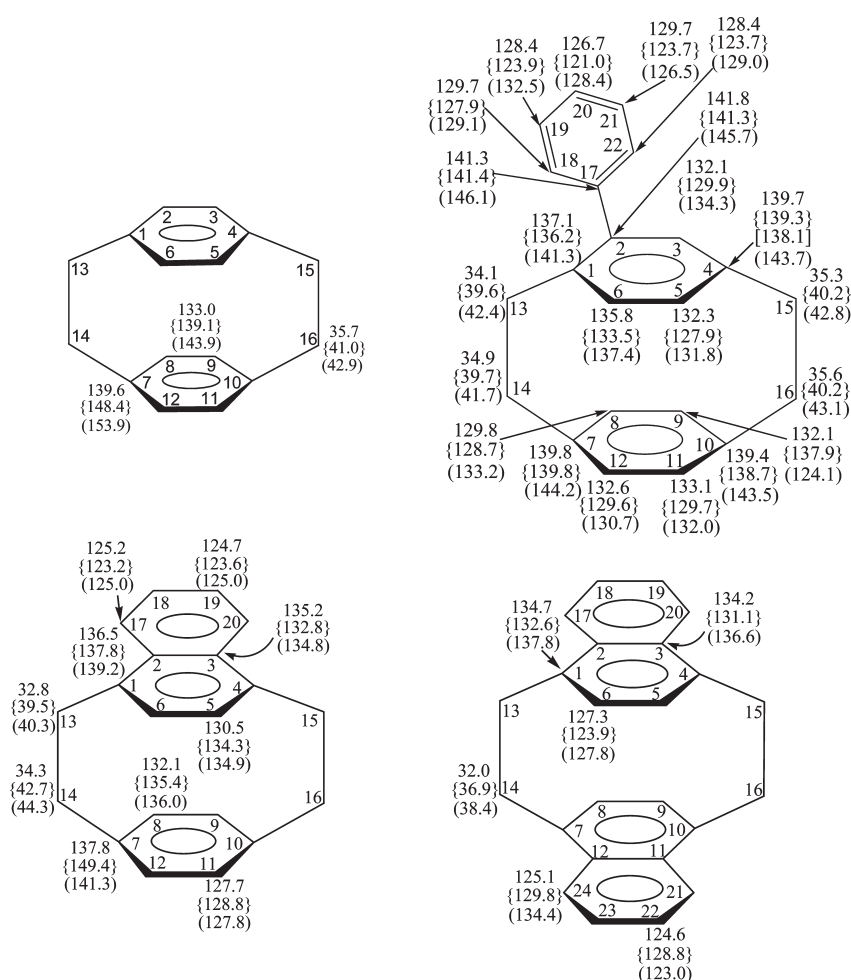


Figure 3. ^{13}C chemical shifts for **1** (upper left), **2** (upper right), **3** (lower left), and **4** (lower right); exp. values, no brackets; calcd using the B3LYP functional are denoted by curly brackets and parentheses for 6-311G(d,p) and Huz-IV basis sets, respectively.

There is a reasonable agreement between the calculated and the experimental values for the torsional angles except for the C1C2C17C22 and C1C13C14C7 angles for **2** (Table SUP-1 in the Supporting Information). The origin of this discrepancy is not clear. Several factors could influence the geometry of this highly strained molecule in the isolated and crystalline state. For example, the X-ray value for the distance between the H13b and the H18 atoms (in the molecular schemes, aliphatic protons in front and behind the drawing plane are labeled a and b, respectively) is 2.281 Å, well below the sum of the van der Waals radii for hydrogen atoms. The calculated torsional angles in the aliphatic bridges in **1–4** will be discussed later, in the context of the temperature effects on the relevant vicinal J_{HH} couplings.

NMR Parameters. The experimental and calculated (at the B3LYP/6-311G(d,p) and B3LYP/Huz-IV levels) proton and carbon chemical shifts values are collected in Figures 2 and 3, respectively. The proton and carbon chemical shifts in **1** were calculated also for the KT1 and KT2 functionals developed especially to describe proton chemical shifts.^{49–51} The results are collected in Table SUP-2 of the Supporting Information together with the corresponding experimental values. The data reveal that the KT1 and KT2 functionals designed to give correct σ_{H} and σ_{C} values are not better than the B3LYP one, although this may be due to the possible deficiencies in the structures predicted by the KT1 and KT2 functionals. Therefore, they have not been used for

the whole series under investigation. A selection of the coupling constants through two and three and more bonds is presented in Tables SUP-3–SUP-7 of the Supporting Information.

Proton Chemical Shifts. The experimental value of the aromatic proton signal of 7.046 ppm for xylene ([http://en.wikipedia.org/wiki/P-Xylene_\(data_page\)](http://en.wikipedia.org/wiki/P-Xylene_(data_page))) is shifted upfield to 6.475 ppm for **1** and split for **2** (6.513–6.642 ppm). The proton chemical shifts of the phenyl substituent are larger by almost 1 ppm than the corresponding values for the aromatic cyclophane signals. For molecules **3** and **4**, the influence of one ring current on the other ring signals is more diversified. The resonances of H9 in the two latter cyclophanes are shifted considerably upfield, to 5.506 and 5.756 ppm, while the change is smaller for the H6 proton in **3** (6.803 ppm). On the other hand, the signals of the naphthalene protons of the outer rings (H17–H24) are shifted to 7.405 and 7.728 ppm, downfield relative to the corresponding xylene value given above. For the aliphatic proton signals, their chemical shifts are 3.072 ppm for **1**, whereas for *p*-xylene they absorb at about 2.296 ppm. For obvious reasons, the presence of the aromatic substituent in **2** changes the proton signals on the bridge more distanced from it very little, but it differentiates considerably between the proton signals of the closer ethylene bridge. In particular, the signal of the H13b proton closer to the phenyl substituent has moved from 3.072 ppm in **1** to 3.438 ppm in **2**, while the chemical shifts

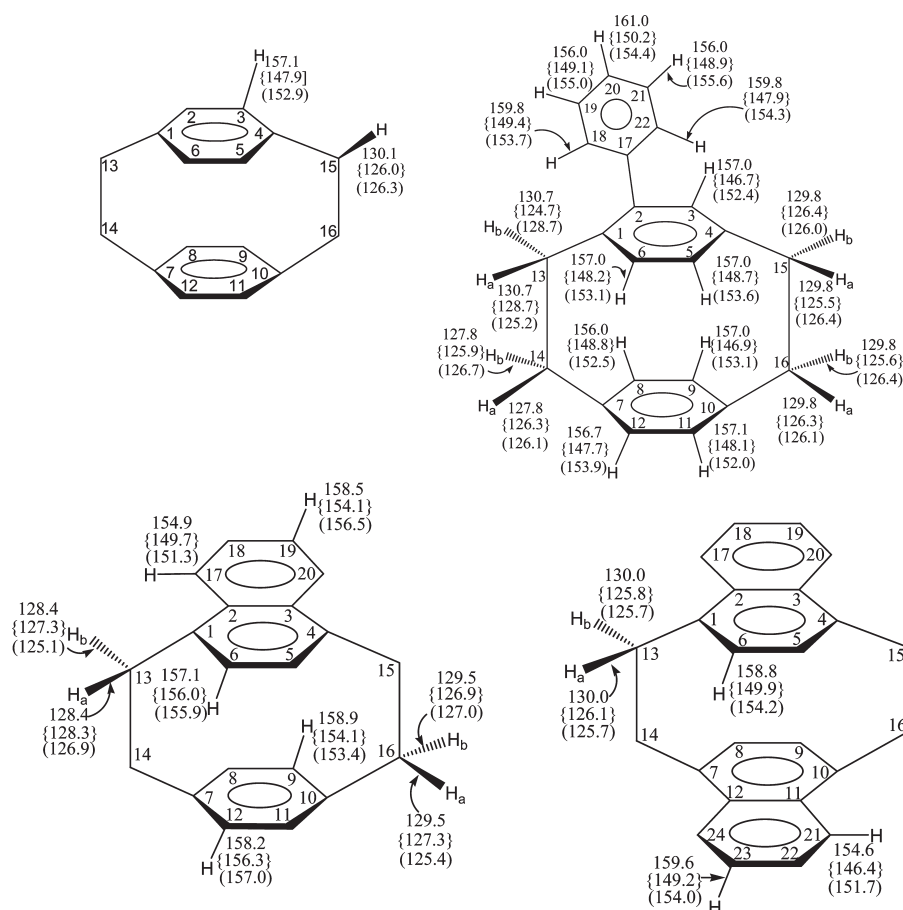


Figure 4. $^1J_{CH}$ coupling constants for 1 (upper left), 2 (upper right), 3 (lower left), and 4 (lower right); exp. values, no brackets; calcd using the B3LYP functional are denoted by curly brackets and parentheses for 6-311G(d,p) and Huz-IV basis sets, respectively.

of the signals of the other protons on the C13C14 bridge changed to the values of 2.671–3.174 ppm. In the latter cyclophane, the chemical shift of the signal of the H13b proton closer to the outer aromatic ring is larger than that of the more distant H13a proton (3.438 vs 2.933 ppm). The same behavior is observed in 3 and 4. The variation of the chemical shifts for the H14 protons in 2 and 3 is much smaller and exhibits the opposite trend.

It should be emphasized that in almost all cases the calculated chemical shifts follow the experimental trends. The few differences that exist are small and thus insignificant. With few exceptions, for most of the signals of the aliphatic protons (CH13 for 1, some for 2, CH12 for 3, and CH13, CH21, and CH22 for 4), the calculated chemical shifts give smaller, mostly insignificantly different, values from the experimental ones.

Carbon Chemical Shifts. A comparison between the experimental values for the signal positions of the parent [2.2]paracyclophane 1 is presented in Figure 3, and the corresponding *p*-xylene values of 134.66, 128.97, and 20.90 ppm ([http://en.wikipedia.org/wiki/P-Xylene_\(data_page\)](http://en.wikipedia.org/wiki/P-Xylene_(data_page))) reveals considerable differences due to both the nonplanar distortions of the aromatic rings and the small separation of the rings. The calculated values presented in Figure 3 are all larger than the experimental ones and roughly correctly describe the experimental trends, namely, that for 2 the largest chemical shifts of over 140 ppm have been both measured and calculated for the C2

and C17 atoms. The second largest values have been obtained for the bridgehead C1, C4, C7, and C10 atoms. The three latter carbon atom positions were only slightly changed in comparison to the corresponding values for the parent compound 1. However, in addition to a considerable change in the position of the C2 carbon atom, the largest differences between 1 and 2 due to the presence of the aromatic substituent at the C2 position manifest themselves at the C1, C6, C13, C14, and interestingly, at the C8 carbon positions. The positions of the signals for the other aromatic carbons of the cyclophane skeleton in the two molecules are only slightly shifted, as is also the case of the aliphatic signals of the C15 and C16 atoms situated at a larger distance from the substituent.

The presence of one or two additional aromatic rings in the cyclophane skeleton in 3 and 4, respectively, causes considerable lowering of all carbon signal positions with the largest effect observed for C18, C17, and C11 of 3 (124.7, 125.2, and 127.7 ppm, respectively) and practically the same lowering (to 124.6 and 125.1 ppm) found for C17 and C18 in 4. A considerable upfield shift of the C5 atom signal should be noted, from 130.5 ppm in 3 down to 127.3 ppm in 4. Smaller shifts were found for the other aromatic carbon atoms. As for 2, the position of the C13 signal close to the aromatic substituent was decreased in 3 and 4. Except for few values where the differences are small, the chemical shifts calculated with the B3LYP functional using the 6-311G(d,p) and Huz-IV basis sets reproduce the trends in the experimental results, with the Huz-IV basis set yielding the

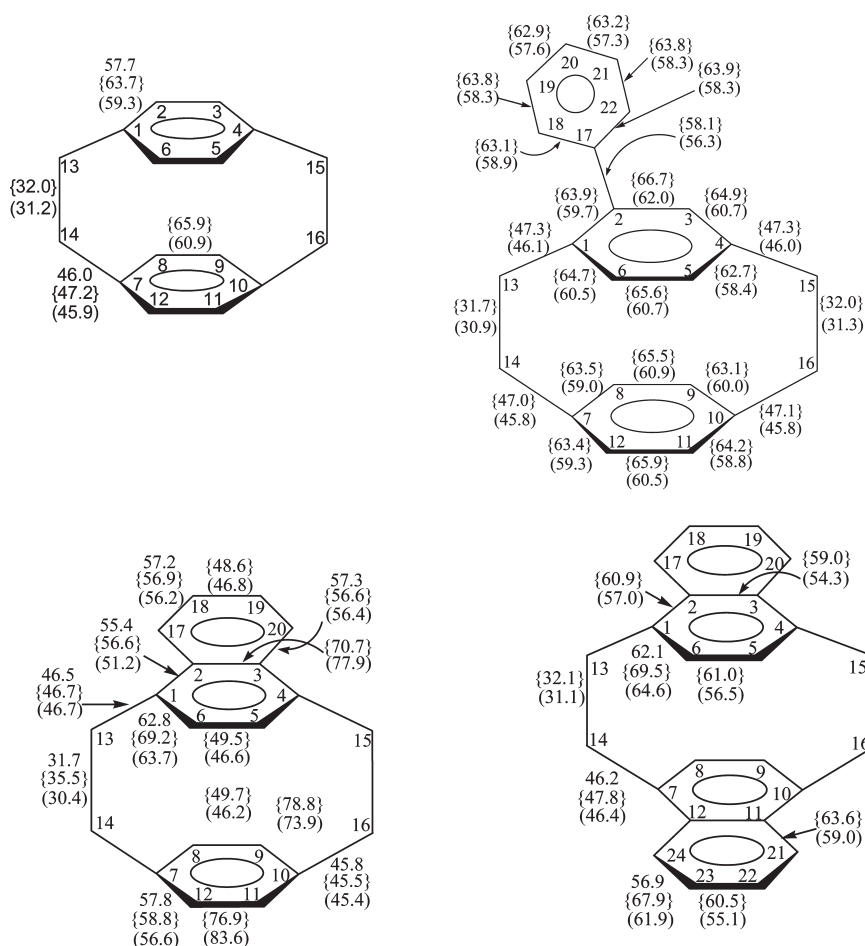


Figure 5. $^1J_{CC}$ coupling constants for **1** (upper left), **2** (upper right), **3** (lower left), and **4** (lower right); exp. values, no brackets; calcd using the B3LYP functional are denoted by curly brackets and parentheses for 6-311G(d,p) and Huz-IV basis sets, respectively.

largest carbon chemical shift values. In contrast to the results calculated for **1** and **2**, where most of the calculated values were larger than the experimental ones, several chemical shifts calculated using the 6-311G(d,p) basis set were smaller than the experimental values for molecules **3** and **4**.

Comparison of the Calculated Chemical Shifts of Model Systems with the Experimental Values for *p*-Xylene and [2.2]Paracyclophane. To analyze the influence of the aromatic ring distortion from planarity and that of the proximity of the aromatic rings in the [2.2]paracyclophane derivatives on the proton and carbon chemical shifts for the molecules under investigation, two series of model calculations have been carried out. The induced chemical shifts in planar and boat-like benzene was calculated first. Then, the shifts of *para*-xylene dimer with distances between the aromatic rings equal to 3.0 and 4.0 Å were calculated. The calculated values are summarized in Tables SUP-8 and SUP-9 of the Supporting Information together with the corresponding experimental values. An inspection of the data in the tables reveals that the trends in carbon chemical shifts are correctly described both by nonplanar distortions of the benzene rings and by the close proximity of the two rings. The change in the chemical shifts of the aliphatic protons in [2.2]paracyclophane as compared to that in *para*-xylene can be also explained by the proximity of the rings. However, the models applied are too crude to fully explain the behavior of the aromatic H2 proton.

J_{CH} and J_{CC} Coupling Constants. The experimental and calculated (at the B3LYP/6-311G(d,p) and B3LYP/Huz-IV levels of theory) $^1J_{CH}$ and $^1J_{CC}$ coupling constants are presented in Figures 4 and 5, respectively.

1J Coupling Constants. The experimental results for the $^1J_{CH}$ of the aromatic rings of the cyclophane skeleton (Figure 4) are only slightly changed within the series of the molecules under study. Small but significant differences of less than 2.3 Hz for the C17H17, C8H8, C9H9, and C19H19 couplings for **3**, of ca. 2.5 Hz for the C17H17 and C18H18 bonds and of ca. 1 Hz for C8H8 for **2** have been observed. For the experimental values of the coupling constants involving the aliphatic protons, there are only small changes of less than 2 Hz within the series **1–4** with practically no difference between the $^1J_{C13H13}$ values for **1** and **4**. Small but significant differences have been observed between the spin–spin couplings involving C13 and C14 in **2** and **4**. However, the differences between the values of the constants involving protons on C13 (and C14) closer or more distant to the substituent on the [2.2]cyclophane skeleton could not be experimentally observed.

All calculated values of $^1J_{CH}$ are lower than the experimental ones. In most cases the values calculated using the Huz-IV basis set are the largest; the calculations with the other basis set do not show such a well-defined trend. With very few exceptions ($^1J_{C9H9}$, $^1J_{C17H17}$, and $^1J_{C19H19}$), the Huz-IV values reproduce the experimental data much better than the values calculated

using the other basis set. For the aliphatic bonds, the 6-311G(d,p) basis set sometimes reproduces the experimental values better, but the differences between the Huz-IV and the latter basis set are small. This is in agreement with the known observation of spin–spin coupling constants being much more sensitive to the quality of the basis set used than are the nuclear shielding constants.⁵⁸

No carbon–carbon coupling constants through one bond could be measured for **2**, see $^1J_{CC}$ (Figure 5). Also for **3** and **4**, some constants could not be determined. Of the measured constants for the former molecule, high values were measured for the C1C2, C1C6, C2C17, and C17C18 couplings, and especially, those for C1C6 and C17C18 for the latter molecule should be noted. Interestingly, in contrast to most observations of $^1J_{CH}$, the measured values are not always larger than the calculated ones. No significant differences (of over ca. 1 Hz) in the calculated values of $^1J_{CC}$ coupling constants between **1** and **2** have been found. Somewhat surprisingly, the large values of ca. 76.9 and 70.7 Hz of $^1J_{C8C9}$ and $^1J_{C2C3}$, respectively, for **3** were calculated using the 6-311G(d,p) basis set, with the considerably larger values obtained using the Huz-IV basis set. Interestingly, the calculated values for $^1J_{C2C3}$ for **4** were lower than 60 Hz. Similarly, the calculated values involving C5C6, C11C12, and C18C19 in **3** dropped below 50 Hz, while the corresponding values for **1** and **2** fall above 60 Hz. Although these values could not be confirmed experimentally, such strong shifts obtained using two different basis sets are consistent with the known basis set dependence of spin–spin coupling constants.

nJ Coupling Constants. Only a few values of $^nJ_{CH}$ ($n = 2–5$) (Table SUP-6 of the Supporting Information) and no $^nJ_{CC}$ couplings could be measured. Theoretical $^nJ_{CC}$ values are given in Table SUP-7 of the Supporting Information. The values of $^2J_{CH}$ involving both aromatic carbon and proton atoms are negligibly small (only $^2J_{C2H17}$ and $^2J_{C3H20}$ are equal to ca. 2 Hz); those involving only aliphatic carbon and proton atoms assume intermediate values of 2–3.6 Hz, while those describing mixed aromatic carbon atoms/aliphatic protons are the largest (3.8–5.9 Hz). Independently of the hybridization of the atoms involved, most calculated values of $^2J_{CC}$ are small, below 2 Hz, with only one reaching about 3 Hz.

As is well-known, the $^3J_{CH}$ values are generally larger than $^2J_{CH}$ ones. For **1–4**, the situation is similar. For instance, the calculated $^3J_{C18H20}$ and $^3J_{C19H17}$ values exceed 9 Hz. Three values of ca. 6 Hz could be measured but not assigned for $^nJ_{CH}$. Several such values were obtained by the calculations.

Of the $^3J_{CC}$ values, the largest ones observed are between the aromatic atoms in the *cis*-arrangement, intermediate ones characterize the planar (or close to planar) *trans*-arrangement of $C_{sp2}C_{sp2}C_{sp2}C_{sp2}$ or of $C_{sp2}C_{sp2}C_{sp2}C_{sp3}$ atoms, the lowest values obtained for the almost perpendicular $C_{sp2}C_{sp2}C_{sp3}C_{sp3}$ fragments.

J_{HH} Coupling Constants in the Aromatic Rings. The J_{HH} coupling values in the aromatic bridges in **1–4** were either evaluated on the basis of the line-shape fits or, in cases where the resonances of the aromatic protons were singlets, read from splittings in the ^{13}C satellites. In the numerical analysis of the AA'BB' system of protons H8, H9, H11, and H12 in **3**, fixed values of J_{H8H9} and J_{H11H12} read from the ^{13}C satellites were used. With these two parameters included in the optimized set, the fitting algorithm did not converge. With two exceptions, the J_{HH} values calculated using the Huz IV basis set reproduce the experimental values best, with a root-mean-square (rms) error of

less than 0.4 Hz. For the 6-311G(d,p) basis set, the error is twice as large. The relevant data are given in Tables SUP-4 and -5 of the Supporting Information.

The two exceptions observed in terms of agreement with experiment involve two couplings in the naphthalene moiety in **3**, J_{H5H6} and J_{H18H19} . For these couplings, the error exceeds 2.5 Hz, regardless of the basis set used. Interestingly, in **4** the corresponding couplings are fairly well-reproduced by the calculations. An inaccuracy in the geometry optimization for **3** cannot be blamed for the discrepancy because the optimized geometries of the naphthalene moieties in **3** and **4** show practically no differences.

Temperature Effects on J_{HH} Coupling Constants in the Aliphatic Bridges. Except for the geminal $^2J_{H13aH13b}$ coupling in **1** (see below), all of the above-mentioned J_{HH} values (Tables SUP-4 and 5 of the Supporting Information) could be extracted from room-temperature spectra with very high accuracy, generally 0.01 Hz, using our own fitting program. For **1**, the vicinal $^3J_{HH}$ couplings were extracted from fits to the multiplets of the ^{13}C satellites of the aliphatic proton singlet. In the fits, the values of the geminal $^2J_{H13aH13b}$ and $^2J_{H14aH14b}$ had to be fixed. They were assumed to be -13.30 Hz, an average of the geminal coupling constants in **2–4**, where they practically do not change within the series. Changes of these values by ± 0.30 Hz have no influence on the fit results for **1**.

Vicinal $^3J_{HH}$ couplings in substituted ethanes are known to be highly sensitive to the dihedral angles involved. Discussion of the $^3J_{HH}$ values will be preceded by a detailed presentation of the relevant structure factors for **2–4**, obtained in calculations using the B3LYP/Huz-IV method. As for **1**, the optimum structures of **3** and **4** show practically no mutual twist of the benzene rings of the cyclophane skeleton, with the corresponding effective symmetry groups being C_s and C_{2h} , respectively. Nevertheless, at variance with the theoretical structure of **1** obtained by us, but in agreement with expectations, in **3** and **4** the aliphatic C–H bonds are twisted off the eclipsed arrangement, with the dihedral angles $\phi_{H13aCCH14a} = \phi_{H13bCCH14b} = 20.7^\circ$ in **4** and with $\phi_{H13aCCH14a} = 14.0^\circ$ and $\phi_{H13bCCH14b} = 14.7^\circ$ in **3**. Only in the calculated structure of **2** the benzene rings in the cyclophane skeleton are considerably twisted, which is a result of steric repulsions between the CH13b and the phenyl moieties. A complete set of optimized dihedral angles in the aliphatic bridges in **1–4** is given in Table 2, with the corresponding graphical illustration shown in Figure 6.

In Table 2, these vicinal coupling values are presented together with the theoretical values and the corresponding optimized dihedral angles. Here, regardless of the basis set used, the theoretical reproduction of the experimental values is rather poor, with a rms error of about 1.30 Hz for each basis set. Interestingly, for the theoretical dihedral angles the phenomenological Karplus equation⁵³ in its canonical parametrization by Haasnoot and De Leeuw⁵⁴ gives a better reproduction of the experimental values, with a rms error of 1.0 Hz only. The results obtained from the Karplus equation are also given in Table 2, including both the J values calculated for the theoretical angles and the torsional angles calculated from the experimental J values. The relatively poor performance of the quantum chemical calculations might originate from the flexibility of the relevant molecular fragments. As pointed out in the Introduction, the occurrence in **1** of low-frequency modes engaging dihedral angles in the ethano bridges appears unquestionable (c.f. ref 11). The amplitudes of the relevant motions should be rather large

Table 2. A Comparison of the Experimental and Calculated Vicinal Coupling Constants (in Hz) between the Aliphatic Protons in 1–4 Obtained from B3LYP/6-311G(d,p) and B3LYP/Huz-IV Levels, Denoted by Curly Brackets and Parentheses Respectively, and the Dihedral Angles (in Degrees) Calculated at the B3LYP/Huz-IV Level, with the Corresponding Values Evaluated from the Karplus Equation^{53,54}

3J	exp.	calcd	$^3J_{\text{Karplus}}$ (ϕ_{calcd})	ϕ_{calcd}	ϕ_{Karplus} ($^3J_{\text{exp.}}$)
1					
H13aH14a	10.65 ± 0.02 ^a	{10.5} (11.4)	11.04	0.0	11
H13aH14b	4.15 ± 0.02 ^a	{2.1} (2.6)	3.22	115.1	121
2					
H13aH14a	10.25 ^a 10.3 ^b	{10.0} (10.2)	10.01	18.0	16
H13aH14b	5.09 ^a 4.7 ^b	{5.3} (6.4)	6.70	133.1	126
H13bH14a	3.79 ^a 3.4 ^b	{0.9} (0.8)	1.05	−96.7	−118
H13bH14b	10.00 ^a 10.0 ^b	{9.7} (10.6)	9.97	18.4	19
H15aH16a	10.69 ^a 10.0 ^b	{10.2} (10.8)	10.58	11.9	11
H15aH16b	3.56 ^a 3.4 ^b	{0.8} (0.6)	1.60	−103.2	−117
H15bH16a	4.59 ^a 4.7 ^b	{4.3} (5.5)	5.19	127.1	123
H15bH16b	10.63 ^a 10.3 ^b	{10.2} (10.8)	10.58	11.9	12
3					
H13aH14a	10.77 ^a	{10.7} (10.8)	10.41	14.0	12
H13aH14b	6.24 ^a	{4.2} (4.5)	5.62	129.2	131
H13bH14a	2.02 ^a	{1.9} (2.1)	1.32	−100.6	−106
H13bH14b	10.27 ^a	{11.2} (11.3)	10.34	14.7	16
4					
H13aH14a	10.09 ^a	{9.7} (10.2)	9.70	20.7	18
H13aH14b	7.54 ^a	{5.9} (6.7)	6.92	135.5	138
H13bH14a	0.98 ^a	{0.7} (0.7)	1.01	−94.0	−96

^a This work. ^b Reference 28.

and would decrease with decreasing temperature. This, in turn, might be reflected in changes of the $^3J_{\text{HH}}$ couplings in the bridges, due to temperature-dependent vibrational corrections to these couplings.⁵⁵ We also note that zero-point vibrational corrections to spin–spin coupling constants may be substantial.⁵⁶ For 1–4, we measured variable-temperature NMR spectra in the

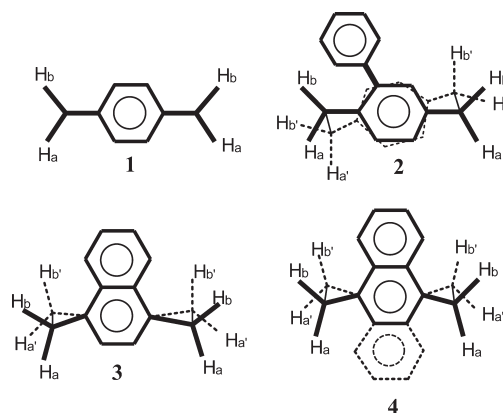


Figure 6. Optimum structures of the ethano bridges in 1–4, calculated using the B3LYP/Huz-IV method.

range 230–326 K. Except for 4, the values of the relevant couplings, extracted with high accuracy from fits to the spectra, do show dependence on temperature although these effects are generally small. The most pronounced effects occur for J_{H13aH14b} in 3 whose values monotonically drop from 2.11 Hz at 326 K to 1.68 Hz at 230 K. In the same temperature interval, the values of J_{H13bH14a} show the reverse trend with a total range of 0.23 Hz. The values of J_{H13aH14a} and J_{H13bH14b} also behave regularly, both decreasing with temperature by about 0.13 Hz in the interval explored. The geminal couplings J_{H13aH13b} and J_{H14aH14b} fluctuate in the interval of 0.04 Hz, which is less than three times the maximum standard errors delivered by the fitting program for each of these couplings (0.02 Hz in each case). In general, we consider a given coupling constant to be temperature-independent if its total range of changes falls below three times its maximum standard error (which usually peaks at the lowest temperature investigated). In this sense, for the staggered arrangements (with $|\phi_{\text{calc}}|$ of Table 2 in the limits of 90–135°) all but two of the vicinal couplings (J_{H13aH14b} and J_{H15bH16a} in 2) in the aliphatic bridges in 1–3 are temperature-dependent. In 4, the situation is unclear because the total ranges of change barely exceeds the assumed thresholds. For the nearly eclipsed positioning of the CH bonds ($|\phi_{\text{calc}}| \leq 21^\circ$), except for J_{H13aH14a} in 4, and J_{H15aH16a} and J_{H15bH16b} in 2, all of the remaining vicinal couplings show small but consistent drop with increasing temperature, by 0.12–0.20 Hz in total, which must be considered a real effect considering the smallness, less than 0.02 Hz, of the standard errors obtained. Except for J_{H16aH16b} in 2, the geminal couplings in 2–4 are temperature-independent, as are the aromatic J_{HH} couplings in these compounds. The geminal and aromatic J_{HH} couplings in 1 could not be measured with sufficient accuracy to assess their temperature behavior.

The observed temperature dependences confirm unequivocally the existence in 1–3 of at least one low-frequency mode that affects the values of vicinal J_{HH} couplings in the aliphatic bridges, leaving the remaining J_{HH} couplings insensitive to temperature. For the eclipsed arrangements, the Karplus curve has a local maximum of about 11 Hz. Therefore, a consistent drop with increasing temperature of the vicinal couplings for the (nearly) eclipsed pairs of CH bonds would mean a progressive opening of the corresponding dihedral angles. Such a behavior could be affected by the twisting-rocking mode described in ref 11 (see Figure 7).

For the couplings involving staggered pairs of CH bonds in 3, which show the most pronounced dependence on temperature,

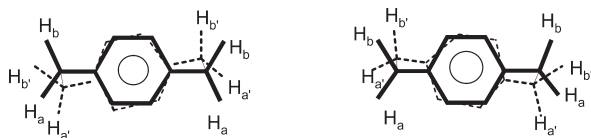


Figure 7. Twisting–rocking mode in **1** (adapted from ref 11).

the simple explanation for their behavior in terms of changes with temperature of the corresponding dihedral angles does not seem possible. The same applies to the behavior of J_{H13aH14b} in **1** (an increase by 0.11 Hz). A proper evaluation of vibrational corrections to these coupling constants would presumably involve calculations of “true” quantum mechanical averages of J for the individual vibrational eigenfunctions of the mode concerned.⁵⁹

The absence of a clear measurable temperature effects in **4** does not necessarily mean that the low-frequency mode considered does not exist in this compound. The moment of inertia for the twisting motion in this molecule is evidently larger than in **3**, and thus delocalization of the vibrational wave functions for the ladder of energy levels of this mode is also reduced as compared to **3**. Tighter localization means smaller changes of the quantum averages of J when switching between different energy levels. Interestingly, the maximum difference between the experimental vicinal couplings in **4** and the values calculated (with no vibrational correction!) using the Huz-IV basis set is only 0.8 Hz, while for **1**, **2**, and **3**, where the vibrational corrections should be appreciable, the respective maximum deviations are 1.5, 2.8, and 1.7 Hz.

CONCLUSIONS

The structure of four [2.2]paracyclophanes were optimized at the B3LYP level (using 6-311G(d,p), Huz-IV basis sets). The calculated structure of the D_{2h} symmetry for the parent molecule agrees with low-temperature X-ray results of the Lyssenko group⁸ but is in strong disagreement with most published calculations.^{19,26} However, in view of the probable occurrence of a low-frequency mode, combining mutual twist of the benzene rings with the rocking of the ethano bridges in **1**, it is difficult to resolve whether the molecule has the D_{2h} eclipsed or D_2 twisted structure.

NMR spectra of the paracyclophanes were measured and chemical shifts and coupling constants determined. In particular, all J_{HH} values, even those less than 0.5 Hz, were measured. The calculations reveal that, in most cases, the 6-311G(d,p) basis reproduces proton chemical shifts best. Such a simple conclusion could not be drawn for the carbon chemical shifts. Except for the values for C13H13a, C14H14a, and C16H16a, the Huz-IV basis set yields the best agreement with experiment for most $^1J_{\text{CH}}$ couplings for **2**. Such correlations have not been noticed for other molecules and basis sets. The influence of the nonplanar benzene ring distortions and their proximity on the carbon and proton chemical shifts was analyzed on the basis of model calculations which showed that the carbon and aliphatic proton chemical shifts are influenced by both effects. However, the modelling could not explain the values observed for the aromatic H2 protons.

In **1–3**, the observed values for the vicinal coupling constants in the aliphatic bridges were found to be temperature-dependent. This provides one argument for the occurrence of a low-frequency twisting/rocking mode in these compounds. In view

of this observation, a comparison of the computed geometries of these compounds with their X-ray structures may be misleading, since the crystal-packing forces might substantially modify the extent of the mutual twist of the molecular moieties.

ASSOCIATED CONTENT

S Supporting Information. Available structural information and NMR parameters of **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

The authors would like to thank the Interdisciplinary Centre for Mathematical and Computational Modelling of Warsaw University for the computational grant G28-7 and the Norwegian Supercomputing Program for a grant for computer time, Grant No. nn4654K. H.D., T.B., and K.R. acknowledge the International Ph.D. Projects Programme of the Foundation for Polish Science, co-financed from European Regional Development Fund within Innovative Economy Operational Programme “Grants for Innovation”. K.R. has also been supported by the Research Council of Norway by research grants Nos. 179568/V30 and 177558/V00. H.D. and L.S.T. gratefully acknowledge support from National Science Council, Taipei.

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