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Distinctive Normal Harmonic Vibrations of [2.2]Paracyclophane

Susan E. Walden and Daniel T. Glatzhofer*

Department of Chemistry and Biochemistry and the Center for Photonic and Electronic Materials and Devices, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019

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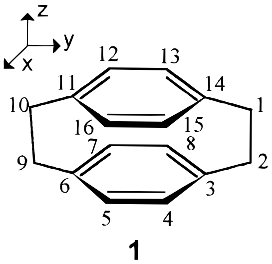
The hybrid Hartree−Fock/density functional method B3LYP and 4-31G(d) basis set were used for geometry optimizations and vibrational analysis of both the D_2 and D_{2h} conformers of [2.2]paracyclophane. The unprecedented full geometry optimization with a split valence basis set and a method that includes electron correlation shows the equilibrium structure of [2.2]paracyclophane to be the twisted D_2 conformation with a calculated twist angle ($C_{ring}C_{bridge}C_{bridge}C_{ring}$) of 3.9°. We present the first complete assignment of all 90 normal harmonic vibrations of [2.2]paracyclophane. Upon examination of the calculated normal modes and comparison with prior assignments for paracyclophanes and *p*-xylene, we have identified vibrations that are cyclophane specific modes. Our calculated harmonic frequencies and relative intensities are in excellent overall agreement with the experimental IR spectrum. We have thus demonstrated the potential of hybrid Hartree−Fock/density functional theory as an electron-correlated method suitable and practical for characterizing even the large, highly strained, structurally and electronically unique parent of the [2.2]paracyclophane family.

Introduction

A very intriguing class of molecules, the [*m.n*]cyclophanes, elicit interest because of their closely spaced and/or conformationally defined benzene rings, the potential interactions between the rings, and the consequences of these features.[1−7] The simplest of these molecules is [2.2]paracyclophane (**1**). With



1

its characteristic two benzene rings held together by two ethano bridges in a para orientation to one another, **1** is the most studied of the family of [2.2]paracyclophanes, as it serves as a model for more chemically diverse derivatives. The ethano bridges constrain the two benzene rings to an inter-ring distance (2.9−3.1 Å) smaller than the sum of their van der Waals radii (3.40 Å). Also as a result of the short bridges, the bridgehead atoms of the benzene rings are bent out of the planes of the remaining carbons. The close spacing and distortion of the benzene rings result in interesting effects on the UV and photoelectron spectra, which have been examined in some detail.[5,8−14] An early study, however, concluded that the vibrational spectrum is not significantly affected by the distortions or inter-ring interactions.[15] Previous calculations of the properties of [2.2]paracyclophane have focused on the UV excitation spectrum and relative ordering of molecular orbitals as predicted by various semiempirical methods.[8,10,12−14] Up until very recently, the most sophisticated computational efforts only included single-point calculations using the X-ray crystal structure with D_{2h} symmetry; however, two recent papers include Hartree−Fock type geometry optimizations of **1** with STO-3G and 3-21G basis sets.[16] Experimentally, the electronic spectra are known to exhibit strong coupling to molecular vibrations.[9,11,16−18] A limited theoretical vibrational analysis based on STO-3G self-consistent-field calculations was reported. There has never been, however, a complete analysis of the vibrational spectrum of **1**. Additionally, correlation energy, known to be important when considering weak interactions or changes in electron pairing,[19,20] has not been accounted for in previous calculations for **1**. We now report the optimized geometry and complete vibrational analysis for **1** calculated using a hybrid Hartree−Fock/density functional method. The method and justification for its use are described next, followed by our computational results.

Computational Methods[19,21,22]

Only recently have ab initio calculations been employed to study properties of [2.2]paracyclophane.[16,23] These studies contained geometry optimizations at the Hartree−Fock level with a minimal STO-3G basis set and the smallest split valence basis set, 3-21G. The energy expression used for Hartree−Fock calculations is

$$E = V_{NN} + H^{core} + V_{ee} + E_X^{\ HF} \qquad (1)$$

where V_{NN} is the nuclear−nuclear repulsion energy, V_{ee} is the Coulombic interaction between electrons, H^{core} is a term for the one-electron kinetic and electron−nuclear interaction energies, and $E_X^{\ HF}$ is the Hartree−Fock exchange term. The Hartree−Fock exchange term treats the repulsive interaction between two electrons as one electron “seeing” the other electron as a smoothed out average of charge. In reality, each electron will have a “donut” around it where the other electron cannot exist so that their positions are not independent but are *correlated*.[19,20] The correlation energy is particularly important when studying systems with weak interactions or where electron pairings will change, for example, van der Waals and charge-transfer complexes, when studying geometry changes from closed to open shell systems, and for determining ionization potentials and pK_a's. Density functional methods include electron correlation by treating electron exchange and correlation energies as functionals of the electron density ρ, *f[g(ρ)]*. Numerous functionals for each, exchange and correlation, exist and are

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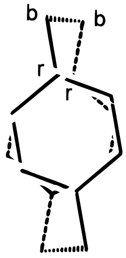
reviewed elsewhere.[24,25] The hybrid Hartree−Fock/gradient-corrected density functional method[19,26] used for this study, B3LYP, is constructed so that the exchange term in (1) is expressed as a three-parameter sum of density functional based exchange and correlation terms and a Hartree−Fock exchange term. This is given by

$$AE_{\mathrm{X}}^{\mathrm{Slater}} + (1-A)E_{\mathrm{X}}^{\mathrm{HF}} + BE_{\mathrm{X}}^{\mathrm{Becke}} + CE_{\mathrm{C}}^{\mathrm{LYP}} + (1-C)E_{\mathrm{C}}^{\mathrm{VWN}} \tag{2}$$

with the three-parameter name coming from the constants A, B, and C, which were determined by fitting the sum to experimental heats of formation. $E_{\mathrm{X}}^{\mathrm{Slater}}$ and $E_{\mathrm{X}}^{\mathrm{Becke}}$ are density functional expressions for exchange energy, based on a local[27] and a gradient-corrected[28] density functional, respectively. $E_{\mathrm{C}}^{\mathrm{VWN}}$ and $E_{\mathrm{C}}^{\mathrm{LYP}}$ are, likewise, expressions for correlation energy in the local density functional approximation (VWN)[29] and with gradient corrections (LYP).[30] The parameters A, B, and C were determined using a different gradient-corrected correlation functional.[26] While this introduces a "parametrized" feature to the method, the high degree of accuracy found for B3LYP with the different correlation functionals and for molecules far removed from the original parametrization set lends support and confidence to the reliability of the method. Although density functional methods have shown great accuracy for closed shell and radical systems,[19,31−39] results for noncovalently bonded systems, especially van der Waals and charge-transfer complexes, show mixed results.[40−43] This should not be a problem as [2.2]paracyclophane is not a van der Waals, or dispersion force dominant, complex. The interactions between stacked, aromatic π-systems are believed to be predominantly Coulombic.[3,44−48] The largest computationally tractable split valence Gaussian basis set with the addition of polarization functions to the heavy atoms, 4-31G(d), was used for this study.[19,49] The program suite Gaussian94 was used for all calculations.[50] The geometry optimizations were accomplished using the default redundant internal coordinates algorithm without any symmetry constraints. The vibrational modes were animated with the program Re_View.[51]

Molecular Geometry

For many years **1** was assumed to adopt a totally eclipsed conformation so that it exhibited D_{2h} symmetry.[5,9,11,15,52] Early X-ray crystal structures supported this concept.[53−55] Even after extensive refinement suggested instead a slightly twisted orientation,[56] calculations of electronic properties of **1** still utilized the D_{2h} conformation.[14] Two independent groups, using Hartree−Fock calculations with STO-3G and 3-21G basis sets, deliberately sought the D_2 twisted structure without success.[16,23] Their calculations repeatedly converged at the D_{2h} geometry. Our calculations at the B3LYP/4-31G(d) level are the first to correctly predict the D_2 twisted conformer as the energy minimum. The first optimization was started at the eclipsed structure where it also converged. This geometry, however, was found to produce one imaginary frequency whose mode corresponded to the two p-xylyl moieties twisting with respect to one another. (One imaginary frequency indicates convergence at a maximum on the potential energy surface, i.e. a transition state. The normal mode associated with the imaginary frequency corresponds to the reaction or molecular coordinate which is changing along that path of the energy surface.) Offsetting the bridgehead carbons by 8° for an additional optimization resulted in a converged structure with a twist angle of 3.9° (shown diagrammatically in **2**). This twist angle compares excellently with the experimentally determined value of 3.2°, from room-temperature X-ray crystallographic measurements.[56] The twisted structure, with approximate D_2 symmetry, produces no imaginary frequencies (see following section). The calculated energy difference between the two structures is only 1×10^{-3} kcal/mol and the twisting vibration is the lowest energy vibration at 22 cm^{-1}, in accordance with experiments suggesting that temperatures below 50 K are required to "freeze-out" the motion.[57] This energy difference is so near the limitations of the method[19] as to be inconclusive regarding the equilibrium structure. Yet, frequency analysis at both geometries and comparison with experiment verify that the D_2 structure, with its very slightly lower energy, is a minimum geometry.



CrCbCbCr angle 3.9°

2

As shown in Figures 1 and 2, bond distances, inter-ring distances, and bond angles are also in very good agreement with experiment. The largest bond length difference is 0.020 Å for the bridge bond versus the average length reported in the experimental paper.[56] The authors of the X-ray structure analysis pointed out that this bond length ranges from 1.579 to 1.604 Å with small variations in the twist angle selected for refinement. At the largest twist angle they used for adjusting bond distances, 3.8° (cf. 3.9° calcd), the difference between calculation and experiment for the bridging bond length is only 0.006 Å. The experimentally determined structure includes nearly identical bond lengths within the six-membered rings, whereas the calculations indicate elongation of the bonds to the bridgehead atoms that are bent out of the plane. The C−C−C bond angles within the rings are identical with experiment within calculational or experimental error. There is some discrepancy in the bond angles involving the methylene hydrogens, but the authors point out that there is substantial uncertainty in the exact positions of the hydrogen atoms. Our calculated geometry indicates that the aromatic hydrogens are bent inward, as was observed in the X-ray crystal structure of **1** as well as the structures of other cyclophanes.[56] That is, the ring hydrogens are approximately 0.04 Å closer together than the two four-carbon planes (decks).

The overestimation of the inter-ring distances versus the experimental values seems to be due to the longer predicted length for the bridge bonds because the three angles defining the ring distortions, α, β, and γ, compare within experimental error to the X-ray-derived structure (Figure 2). The bridging bond length, the inter-ring distances, and degree of twisting away from the eclipsed conformation were hypothesized to be interrelated as opposing forces determining the equilibrium geometry. Though our calculated inter-ring and bridging bond distances deviate more from experiment than is typical for this method, their values are the same for both the D_2 and the D_{2h} structures. This implies that the bond and inter-ring distances are not affected by small twists of the rings. While B3LYP/4-31G(d) calculations overestimate these distances, the Hartree−Fock/STO-3G and 3-21G calculations[23] underestimated the inter-ring distances and slightly overestimated the bridging bond length. It is typical for the hybrid Hartree−Fock/density functional method to predict longer bond lengths than traditional Hartree−

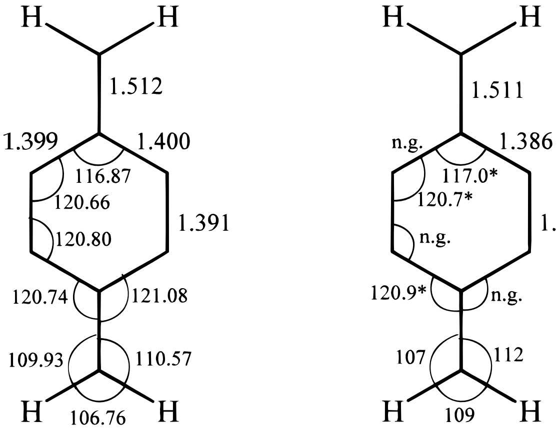
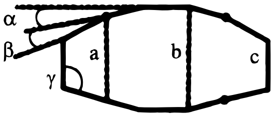


Figure 1. Selected internal coordinates (distances in angstroms and angles in degrees) for half of [2.2]paracyclophane. Calculated using B3LYP/4-31G(d) on left and from X-ray crystal structure on right (ref 56). The calculated structure possesses essentially D_2 symmetry. *These angles were not corrected for the twist distortion. Bond angles and bond distances nonequivalent in D_2 symmetry that are not shown in right structure were not given in the paper (n.g.)



Calculated (a-c in Å, α–γ in deg.) B3LYP/4-31G(d)		Experimental (a-c in Å, α–γ in deg.) Ref. 56	
a	2.820	a	2.78
b	3.138	b	3.09
c	1.610	c*	1.593
α	12.50	α	12.6
β	11.04	β	11.2
γ	113.56	γ	113.7

Figure 2. Selected distances and angles for inter-ring structure. *Only c is corrected for the twist distortion.

Fock calculations, but the excess deviation in our calculations could be an artifact of the relatively small basis set we were required to use. The unfortunate consequence is that this could decrease through-space interactions we are hoping to model; however, any through-space interaction we do observe would then likely be even more significant experimentally. The possibility also exists that in gas-phase measurements, more similar to calculations, the repulsive forces pushing the rings apart would have a greater contribution to molecular geometry than they do in the condensed phase.

In summary, B3LYP/4-31G(d) calculations produce an equilibrium geometry in very good agreement with one determined by X-ray crystallography. These are the only calculations to date that correctly show the D_{2h} structure is a transition state between two noneclipsed, "twisted" conformations. As indicated from heat capacity experiments,[57] the energy barrier for this twist is extremely small.

Vibrational Analysis

Interest in the vibrations of [2.2]paracyclophane has centered on the coupling of the low-frequency vibrations with electronic transitions.[9,11,16−18] The detailed interpretation of this vibronic coupling has been hindered by the lack of thorough descriptions of the harmonic vibrations.[15,16,52,58−60] Experimental characterization of the vibrations is difficult since, although 66 of the 90 vibrations are allowed in the IR, few bands have actually been observed and most of these are quite weak. Even spectra measured on concentrated samples are deceptively simple, with most allowed vibrations hidden in the baseline.[52] Owing to poor solubility and very weak bands, even Raman spectra for **1** are scarce.[15,52] Additionally, the measured bands have symmetries assigned assuming D_{2h} molecular symmetry and normal modes assigned assuming little deviation from *p*-xylene modes.[15,52] Based on Raman spectra, the assertion was made that there is no difference between the force constants for "in-plane" vibrations (what would be in-plane modes if each ring were simply a substituted benzene) of **1** and *p*-xylene.[15] Prior theoretical attempts at elucidating the normal modes consist of semiempirical and STO-3G SCF calculations.[16] Neither split valence basis sets nor electron correlation (beyond AM1-CI) have been attempted for evaluation of vibrational frequencies. As mentioned in the previous sections, these earlier calculations did not accurately produce the D_2 symmetric structure as the minimum conformation. The resulting normal mode analysis could suffer from the symmetry variance.

Extensive assignment of the modes associated with the observed vibrational bands has heretofore not been attempted. The low-frequency vibration most strongly coupled with electronic excitation is generally believed to be the breathing, or concertina, mode estimated at 235−240 cm^{-1}.[11,16,17] One spectral interpretation assigned the 235 cm^{-1} progression to coupling with a twisting normal mode.[18] Opinions also differ on how many vibrations couple with the $S_1 \leftarrow S_0$ transition. One solid-state fluorescence study included a ring C−C stretch of ≈1600 cm^{-1} and identified weaker coupling to vibrations of 50(5), 80(3), and 180(8) cm^{-1},[18] while a subsequent analysis of fluorescence from the supersonic jet determined that coupling exists only with the breathing and twisting modes, using a twisting mode frequency of ~50 cm^{-1}.[16] This twisting mode has been assigned frequencies ranging from 72 cm^{-1} (ref 17) to 33 cm^{-1}.[16] Due to their behavior with additional bridges, four of the 90 normal vibrations have been described as modes associated with ring distortion: 1600, 940, 890, and 720 cm^{-1}, approximately.[58−60] Complete assignment of the remaining 84 vibrations is critical for total, accurate characterization of vibronic coupling in the fluorescence spectrum.

Thus in addition to examining the normal modes for paracyclophane distinctive bands, we present the first complete set of vibrational frequencies with their intensities and corresponding normal mode descriptions. These calculated vibrational modes for D_2 symmetric **1** are compared with the experimental assignments based on the *p*-xylene model with presumed D_{2h} symmetry.[15,52] The calculated modes are analyzed particularly for paracyclophane specific modes, e.g. those modes with considerable mixing of ring and bridge vibrations. Calculated mode descriptions with frequencies (raw and scaled) and intensities are presented in Tables 1−4. Several comparisons have been made of frequencies calculated with B3LYP/6-31G(d) and experimental values for various molecules resulting in recommended scaling factors of ~0.963.[37,38,61] Low-frequency modes, particularly those that would normally be considered out-of-plane modes for an aromatic molecule, are generally much closer to experiment than a 0.963 scale factor implies.[39] In fact a separate scaling factor of 1.0013 was suggested for "low-frequency" modes, though that designation was not defined.[38] The 1.0013 scale factor is applied here to frequencies < 550 cm^{-1}; 0.963 is used for the remaining frequencies. For 39 calculated vibrational frequencies which could be matched with experimentally determined bands of the same symmetry, the average absolute error of the scaled frequencies is only 12.9 cm^{-1}. The frequencies range from 3070 to 243 cm^{-1} (exptl), indicating excellent agreement between our calculations and experiment. Where possible, the mode descriptions are based

TABLE 1: A Symmetric Modes for [2.2]Paracyclophane

freq	scaled[a]	exptl[b]	normal mode description[c]
3178.2	3060		CH stretch (W2) (ip)
3155.0	3038	3044	CH stretch (W7b) (op)
3078.3	2964		CH2 stretch (op)
3057.3	2944	2937	CH2 stretch (ip)
1667.0	1605	1594	ring stretching (W8a) (ip)
1620.1	1560		ring stretching (W8b) (op)
1533	1476		CH2 scissor (ip)
1364.2	1314	1323	ar. CH bend (W3) + small CH2 twist (op)
1306.3	1258		CH2 wagging (op)
1257.5	1211		CH2 twist (ip) + very slight W3, opposite phasing between CH2 and W3 modes as 1314
1225.0	1180	1180	Cr−Cb stretch (W7a) (ip) + Ar. CH bend (W9a) (ip)
1216.5	1172		ar. CH bend (W9a) (ip) + Cr−Cb stretch (W7a) (ip)
1008	971		CH2 rocking + very slight W3
963	928		ar. CH wagging (W17a) (ip)
908	874	905	Cb−Cb stretch + Ar CH wagging (W17b) (op)
856	824		ar. CH wagging (W17b) (op) + ring 'out-of-plane' bending (W16b) (op)
796	766	790	W17b (op) + Cb-Cb stretch + ring breathing (W1) (ip)
652	628	637	ring 'in-plane' bending (W 6b) (op)
584	562	568	W16b + W17b + CrCbCb bending (op)
466	467	465	ring 'in-plane' bending (W6a) (ip)
437	438		ring 'out-of-plane' bending (W16a) (ip)
309	310		CrCrCb bending (W9b) (op)
237	237	243	concertina or breathing
22	22		twist

[a] Raw frequencies > 550 cm^{-1} are scaled by 0.963 (ref 37), and those < 550 cm^{-1} are scaled by 1.0013 (ref 38). [b] Experimental frequencies for [2.2]paracyclophane are taken from symmetry assignments in ref 52. [c] (W#) indicates similarity to Wilson mode # for para-disubstituted benzenes. (ip) and (op) indicate in-phase and out-of-phase vibration with respect to the opposite *p*-xylyl fragment. In-phase is defined as movement in the same direction for pseudoeclipsing atoms. Cr = Cring; Cb = Cbridge (**2**).

TABLE 2: B1 Symmetric Modes for [2.2]Paracyclophane

freq	scaled[a]	IR int.	exptl[b]	normal mode description[c]
3175.7	3058	5.9	3037	CH stretch (W2) (op)
3157.8	3041	0.01		CH stretch (W7b) (ip)
3102.2	2987	0.04		CH2 asymmetric stretch (ip)
3043.4	2931	38.8	2927	CH2 symmetric stretch (op)
1664.4	1603	8.38	1596	ring stretching (W8a) (op)
1624.3	1564	0.00		ring stretching (W8b) (ip) + small CH2 rock (ip)
1510.7	1455	0.49	1440	CH2 scissor (op)
1373.7	1323	3.52	1324	CH2 wagging (ip)
1366.5	1316	0.02		ar. CH bending (W3) (ip) + small CH2 twist (ip)
1221.5	1176	5.50	1180	CrCb stretching (W7a) (op) + very small (W9a) (op)
1215.8	1171	0.01		ar. CH bending (W9a) (op) + very small (W7a) (op)
1200.1	1156	0.01		CH2 twist (op) + very small (W3) (ip)
972.6	937	0.00		ar. CH wagging (W17a) (op)
913.1	879	21.37	896	CrCbCb bending + ring 'out-of-plane' bending (W16b) (ip)+ Ar CH wagging (W17b) (ip)
831.9	801	32.03	807	(W17b) (ip) and (W16b) (ip)
811.4	781	0.91		CH2 rocking (ip)
657.0	633	0.91		ring 'in-plane' bending (W6b) (ip)
652.1	628	18.71	624	same as 879 but phasing between (W17b) (ip) and {(W16b) (ip) + CrCbCb bend}
527.1	528	14.89	510	ring 'in-plane' bending (W6a) (op) + (W16b) (ip)
456.5	457	0.00		ring 'out-of-plane' bending (W16a) (op)
359.1	360	0.00		CbCrCr bending (W9b) (ip)
319.2	320	0.21	304	(W16b) (ip)

[a] Raw frequencies > 550 cm^{-1} are scaled by 0.963 (ref 37), and those < 550 cm^{-1} are scaled by 1.0013 (ref 38). [b] Experimental frequencies for [2.2]paracyclophane are taken from symmetry assignments in ref 52. Modes in that reference of b_{2u} symmetry correspond to our B1 symmetry. [c] (W#) indicates similarity to Wilson mode # for para-disubstituted benzenes. (ip) and (op) indicate in-phase and out-of-phase vibration with respect to the opposite *p*-xylyl fragment. In-phase is defined as movement in the same direction for pseudoeclipsing atoms. Cr = Cring; Cb = Cbridge (**2**).

on the Wilson modes of a para-disubstituted benzene or of benzene, which are indicated by a W# designation.[62] When referring to modes derived from either *in-plane* or *out-of-plane* benzene vibrations, these same traditional descriptors are used. However, because the benzene-like rings of **1** are not planar, the phrases will be enclosed in single quotes when referring specifically to vibrations of **1**. Experimental frequencies for **1** are also given in the tables for reference.

Group theory dictates that the 90 vibrations of **1** reduce to 24 modes of A symmetry and 22 each of B_1, B_2, and B_3 symmetries. Only the B_n modes are allowed vibrations in IR, while all vibrations are Raman active. Although only the 24 A modes correspond to forbidden transitions in IR, an additional 30 modes of B_n symmetry have calculated intensities ≤ 0.14 KM/mol. (These are the units for calculated intensities and this value corresponds to a *very* weak observed intensity.) The total of disallowed and very weak bands, 54, is two less than the number of forbidden IR vibrations under D_{2h} molecular symmetry. This is an interesting coincidence, but of the 36 modes with intensity > 0.25, six are symmetrically forbidden in the IR under D_{2h}. Although the weak intensities for D_2-allowed vibrations may be indicative of the very small distortion of the molecule from D_{2h}, the presence of significantly nonzero, forbidden (D_{2h}) bands implies that D_{2h} symmetry is not an accurate approximation for the vibrations of [2.2]paracyclophane.

Low-frequency modes (<400 cm^{-1}) of **1** may be characteristic of paracyclophanes, as they are dominated by combinations of relative rotations or translations of the entire *p*-xylene, benzene, or ethane subunits. One of these modes has been classified as both a concertina mode and a breathing mode and has been experimentally assigned frequencies ranging from 235 to 241 cm^{-1}.[11,16,17] Our calculations predict this totally symmetric mode at 237 cm^{-1}. Our calculated normal mode does not include contributions from Wilson mode 1, the benzene breathing vibration; instead this normal mode is comprised of out-of-phase[63] translation of the two rings along the *z*-axis that is hindered by the presence of the bridge. Figure 3a shows a side view along the *x*-axis where the "12-membered" ring seems to be "breathing". Assignment of the 237 cm^{-1} vibration to this "breathing" mode is at variance with one experimental study that assigned the 240 cm^{-1} progression in the coupled fluorescence spectrum to a mode comprised of ring twisting.[18] Their assignment as the twist was based on a prediction of the frequency depression from deuterating the ring positions followed by measuring that change. They predicted an isotope effect of 6% for a twist mode and 1.5% for a breathing mode. Their assignment was thus based on the measured frequency decrease of 4.6%. Our calculations substituting deuteria for ring hydrogens predict a decrease of the frequency of the *breathing* mode of 4.6%. Thus their experiment actually supports the assignment of that vibration to the paracyclophane breathing mode.

The paracyclophane twist mode, Figure 3b, garners interest regarding its relationship to the true equilibrium structure. The question has been asked whether the D_2 conformation of **1** is an equilibrium structure or is a result of molecular vibration.[55−57] Interpretation of thermochemical measurements suggested that the twist distortion becomes an active vibration at 50 K (corresponding to $\nu \approx 38$ cm^{-1}).[57] X-ray crystal analysis at

TABLE 3: B2 Symmetric Modes for [2.2]Paracyclophane

freq	scaled[a]	int.	exptl[b]	normal mode description[c]
3171.5	3054	0.01		CH stretch (W20b) (op)
3157.2	3040	48.2	3017	CH stretch (W13) (ip)
3078.4	2965	0.05		CH2 asymmetric stretch (op)
3056.2	2943	181.1	2932	CH2 symmetric stretch (ip)
1562.0	1504	13.5	1505	ring stretching (W19a) (ip)
1532.5	1476	0.89	1445	CH2 scissor (ip)
1463.5	1409	0.02		ring stretching (W19b) (op) + CH2 twist (op)
1340.3	1291	0.13		ring stretching (W14) (op) + CH2 wag (ip)
1301.9	1254	5.2	1230	CH2 wagging (op)
1250.1	1204	0.42		CH2 wagging (ip)
1229.8	1184	0.00		ar. CH bending (W18a) (ip) + small CrCb asymmetric stretch (W20a) (ip)
1149.4	1107	0.01		ar. CH bending (W18b) (op)
1044.3	1006	0.11		ring ‘in-plane’ bending (W12) (ip)
976.8	941	0.26		CH2 rock (op)
959.8	924	9.3	937	ar. CH wagging (W5) (op)
892.7	860	2.4	890	CbCb stretch + small (W5) (op)
811.7	782	0.00		ar. CH wagging (W10a) (ip)
745.6	718	29.1	721	ring ‘out-of-plane’ bending (W4) (op) + CrCbCb bend + CbCb stretch
686.4	661	2.3		CrCb asymmetric stretch (W20a) (ip) + small CrCbCb bend and CbCb stretch
388.9	389	0.88	384	bellows
214.7	215	0.00		bridge rock + ring rock around *y*-axis
77.8	78	0.00		bridge rock + ring rock around *y*-axis, phasing opposite to 215

[a] Raw frequencies > 550 cm^{-1} are scaled by 0.963 (ref 37), and those < 550 cm^{-1} are scaled by 1.0013 (ref 38). [b] Experimental frequencies for [2.2]paracyclophane are taken from symmetry assignments in ref 52. Modes in that reference of b_{1u} symemtry correspond to our B2 symmetry. [c] (W#) indicates similarity to Wilson mode # for para-disubstituted benzenes. (ip) and (op) indicate in-phase and out-of-phase vibration with respect to the opposite *p*-xylyl fragment. In-phase is defined as movement in the same direction for pseudoeclipsing atoms. Cr = Cring; Cb = Cbridge (**2**).

TABLE 4: B3 Symmetric Modes for [2.2]Paracyclophane

freq	scaled[a]	IR int.	exptl[b]	normal mode description[c]
3174.5	3057	97.8	3070	CH stretch (W20b) (ip)
3154.8	3038	0.01		CH stretch (W13) (op)
3102.5	2988	67.0	2956	CH2 asymmetric stretch (ip)
3043.3	2931	0.14		CH2 symmetric stretch (op)
1562.2	1504	0.00		ring stretching (W19a) (op)
1510.4	1455	0.26		CH2 scissor (op)
1469.5	1415	12.2	1415	ring stretching (W19b) (ip) + CH2 twist (op)
1370.8	1320	0.00		CH2 wagging (ip)
1348.9	1299	0.11		ring stretching (W14) + CH2 wag (op)
1230.4	1185	0.00		ar. CH bending (W18a) (op) + small CrCb stretching (W20a) (op)
1195.8	1152	1.78	1170	ar. CH bending (W18b) (ip) + CH2 twist (op)
1126.6	1085	3.77	1089	ar. CH bending (W18b) (ip) + CH2 twist (op) opposite phasing from 1152
1041.9	1003	0.00		ring ‘in-plane’ bending (W12) (op)
967.0	931	0.00		ar. CH wagging (W5) (ip)
843.7	813	2.8	855	ar. CH wagging (W10a) (op) + CH2 rock (op)
827.6	797	0.32		CrCbCb bending (op)
787.3	758	0.34		CH2 rock (ip) + (W10a) (op)
742.9	714	0.00		ring ‘out-of-plane’ (W4) (ip)
538.8	540	0.00		CrCb wagging (W10b) (op)
299.8	300	0.18		CbCrCr bending (W15) (ip)
161.0	161	0.15		ring rock around *y*-axis (op) “clamshell”
156.7	157	0.02		translation of each *p*-xylyl fragment in opposite directions along *y*-axis “slide”

[a] Raw frequencies > 550 cm^{-1} are scaled by 0.963 (ref 37), and those < 550 cm^{-1} are scaled by 1.0013 (ref 38). [b] Experimental frequencies for [2.2]paracyclophane are taken from symmetry assignments in ref 52. [c] (W#) indicates similarity to Wilson mode # for para-disubstituted benzenes. (ip) and (op) indicate in-phase and out-of-phase vibration with respect to the opposite *p*-xylyl fragment. In-phase is defined as movement in the same direction for pseudoeclipsing atoms. Cr = Cring; Cb = Cbridge (**2**).

room temperature, however, also showed this twist distortion in the ground-state geometry of the molecule.[56] Analysis of the jet-cooled fluorescence excitation spectrum assigned the ground-state geometry to D_2 symmetry, the frequency of the twist mode as 72 cm^{-1}, and the barrier for the twist between equivalent D_2 conformations as ≤ 50 cm^{-1}.[17] Our calculated vibrations show two modes consisting of the benzene rings twisting in opposition to one another around the *z*-axis. These are mixed with ethano bridge rocking, which would be equivalent to ethane rotation around the *y*-axis. The in-phase combination of these two rotations is calculated as the lowest energy vibration at 22 cm^{-1} and has been called the “twisting” mode because it appears to be each *p*-xylyl fragment rotating out-of-phase with the other fragment. The out-of-phase combination of the benzene and ethane rotations, which greatly resembles an out-of-phase combination of W9b for each *p*-xylyl fragment, is calculated at 310 cm^{-1}. The calculated vibrational frequency nearest to the 72 cm^{-1} progression hypothesized as being the twist mode is a B_2 mode at 78 cm^{-1}, which is symmetry-forbidden from coupling to the electronic excitation. Illustrated as 3c, this is a combination of ethano rotation and benzene rotation around the *y*-axis, out-of-phase with one another. Although there is little precedent for comparisons of calculated (B3LYP) and experimental frequencies this low in frequency,[37,38] our results suggest that the 72 cm^{-1} progression is not the A symmetric twist mode. An example of a combination of subunit translations is the B_3 symmetric mode at 156.9 cm^{-1}, which is the combination of y and $-y$ translations of *p*-xylene.

It seems intuitive that these very low-frequency vibrations of **1** would resemble combinations of the translations and rotations of the molecular fragments since their frequencies border or overlap the microwave region of the electromagnetic spectrum. These modes which result from motions that would not be vibrations for the *p*-xylene, benzene, or ethane fragments have to be considered characteristic vibrational bands of **1**.

In contrast to *p*-xylene, which has only two strong IR bands in the fingerprint region from 1000 to 300 cm^{-1},[64] four to six bands were experimentally observed for **1**.[15,52] Three of these bands were proposed to result from distortion of the benzene rings since their intensities decrease with increasing bridge lengths. Thus the bands near 940, 890, and 720 cm^{-1} have been attributed to paracyclophane bands.[52,58−60] Our calculations indicate six strong bands in this frequency range.

A very strong B_1 symmetric band near 515 cm^{-1} (510 cm^{-1}, ref 34; 519 cm^{-1}, ref 15) was described as out-of-plane ring deformation, which is somewhat supported by our calculation of the normal mode at 528 cm^{-1} as having W16b character with the ring deformation of each deck in-phase (Figure 3d). The out-of-phase combination of the ‘in-plane’ Wilson mode W6a also contributes significantly to this vibration, however. The W6a in-phase mode shows virtually no mixing with other vibrations. In contrast, the calculated out-of-phase combination of W16b for the two rings is no longer mixed with W6a, but instead is found primarily as the A mode at 562 cm^{-1} mixed with $C_{bridge}-C_{bridge}$ (CbCb) stretching and CH wagging. Wilson numbered mode W16b describes a boat deformation of benzene. As the benzene rings of **1** are already distorted into a boat conformation, it is not surprising that this local mode mixes extensively in the calculated vibrations. It is found as a contributor to 4 A and 4 B_1 modes ranging from 562 to 874 cm^{-1} and from 320 to 880 cm^{-1}, respectively. With one exception, the frequencies of these combined vibrations are

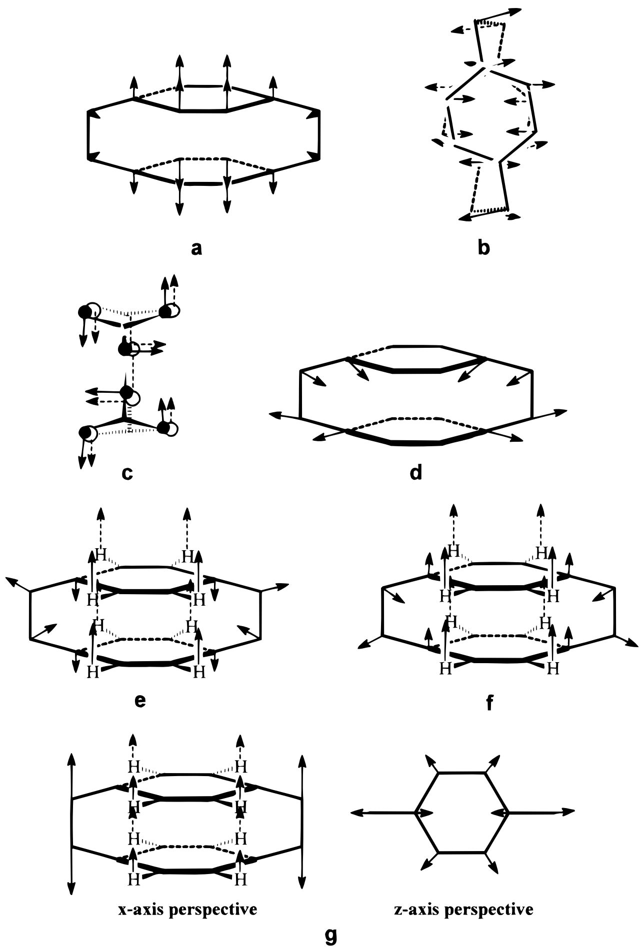


Figure 3. Selected normal modes for **1** from B3LYP/4-31G(d) calculations: (a) A symmetry (sym), 237 cm^{-1}; (b) A sym, 22 cm^{-1}; (c) B2 sym, 78 cm^{-1}; (d) B1 sym, 528 cm^{-1}; (e) B1 sym, 628 cm^{-1}; (f) B1 sym, 879 cm^{-1}; (g) A sym, 766 cm^{-1}.

higher than the W16b mode for *p*-xylene, 483 cm^{-1} (exptl) and 501 cm^{-1} (calcd).

The intense band near 625 cm^{-1} (624 cm^{-1}, b_{2u}, ref 34; 627 cm^{-1}, ref 15) was assigned by Schettino and co-workers to in-plane ring deformation. Indeed the two modes nearest in frequency for *p*-xylene are in-plane ring bending. The prior assignment also described this band as the out-of-phase combination of vibrations whose in-phase combination is the Raman-observed, a_g symmetric, band at 637 cm^{-1}. Our calculations disagree with both assertions for this band. The very strong band near 625 cm^{-1} with a calculated frequency of 628 cm^{-1} and B_1 symmetry is now described as a combination of mostly W17b and $C_{ring}-C_{bridge}-C_{bridge}$ (CrCbCb) bending with some W16b (Figure 3e). Wilson mode W17b is symmetric wagging of the aromatic CH's, which, like W16b, corresponds to a deformation relative to benzene that is already present in the equilibrium geometry of **1**. Also like W16b, W17b is found in 7 A or B_1 modes between 320 and 879 cm^{-1}. These vibrations are in-phase between decks in this band and in another very strong band calculated at 879 cm^{-1}. These two modes differ in the relative phasing between the CrCbCb bending and the CH wagging. There is not an exactly correlating A symmetric mode for this combination of vibrations. The calculated A mode near the experimental 637 cm^{-1} band is an 'in-plane' deformation (W6b) calculated to occur at 628 cm^{-1}. This interpretation for the A mode is supported by Raman assignments.[15]

The mode calculated at 879 cm^{-1} seems to correspond to the very strong band observed near 900 cm^{-1}.[52] It is not clear if this very strong peak observed by those authors in the spectrum of the isotropic polycrystalline sample is assigned to their b_{2u} mode of 896 cm^{-1} or their b_{3u} mode of 905 cm^{-1}. The b_{2u} mode is proposed to be ring stretching, whereas the b_{3u} mode is described as CH wagging. The calculated normal mode at 879 cm^{-1} of B_1 symmetry is predicted to have 'out-of-plane' character like the b_{3u} band but is correlated in symmetry with the b_{2u} band (Figure 3f). With significant contribution from CrCbCb bending, this band is expected to be greatly altered by increasing the bridge lengths, as was observed in experiments. The other b_{2u} (B_1) symmetric strong IR band is found near 805 cm^{-1} (807 cm^{-1}, ref 34; 809 cm^{-1}, ref 15; 801 cm^{-1}, calculated). This mode was described by both Schettino and Scudder as CH wagging. Our calculated vibration is predominately W17b, but with significant W16b contributions as well.

The remaining two strong vibrations in the fingerprint region are two of the bands characterized as changing with differing bridge lengths or arising from the distorted benzene rings. These were assigned by Schettino and co-workers to b_{1u} skeletal modes at 937 and 721 cm^{-1}.[52] Scudder et al. elaborated on these assignments, referring to a strong band at 723 cm^{-1} as a strongly mechanically coupled out-of-phase combination of Wilson mode W4.[15] Mode W4 can be pictured as a chair deformation of benzene. The vibration as calculated is W4 out-of-phase between the two decks and mixed with CrCbCb bending and CbCb stretching. The only strong IR active vibration calculated near 937 cm^{-1} is a B_2 band at 924 cm^{-1}. Although the symmetry is the same as determined from the IR spectra with polarized light, the description of the mode offered here differs from the previous one. We assign this band as Wilson mode W5, a CH wagging mode, out-of-phase between the rings. Another B_2 band, but with very weak calculated intensity, is predicted at 940 cm^{-1} with a normal mode description of CH_2 rock. Since the intensities are so different, we choose to correlate the calculated band at 924 cm^{-1} with the experimentally observed band. W5 is not an IR-allowed mode for *p*-xylene, and its intensity dependence on bridge length may be related to mechanical coupling between the rings, as was hypothesized for W4.

The two most intense bands in the Raman spectrum of **1** are at 156 and 790 cm^{-1}.[15] We offer the first assignment for the band at 156 cm^{-1}, describing it as a "sliding" mode. It is pictured as one-half (one *p*-xylyl unit) of the molecule translating in the opposite direction of the other half along the "long-axis". The band observed at 790 cm^{-1} was assigned to Wilson mode W1, the benzene breathing mode, due to its close proximity to W1 for *p*-xylene (830 cm^{-1}).[15] Under the assumption that A symmetric modes would be most intense in the Raman spectrum,[52] this band corresponds to a calculated frequency of 766 cm^{-1} with a complex normal mode description (Figure 3g). The vibration is a combination of W17b, W1, and Cb$-$Cb stretching. Movement of the benzene ring carbons is reminiscent of W1, an 'in-plane' mode; yet there is also 'out-of-plane' wagging of the aromatic hydrogens and significant stretching of the bridge bonds. This 'breathing' mode is different from the one near 240 cm^{-1} because the bridges are stretching and the distance between the four-carbon planes of the six-membered rings is not changing (cf. 3a and 3g). While the 790 cm^{-1} band can certainly be termed a paracyclophane breathing mode, with mixing between 'in-plane' and 'out-of-plane' contributions, it cannot accurately be called Wilson mode 1.

In the spectral region where CH_2 bending, aromatic CH bending, and ring stretching are expected to occur, 1050$-$1600 cm^{-1}, **1** shows several deviations from historical assignments for *p*-xylene as compiled by Varsanyi.[64] Most of these differences in assignment are also indicated by our calculations

TABLE 5: Direct Comparison of Calculated Frequencies (cm^{-1}) for the Wilson Modes of [2.2]Paracyclophane with Calculated and Experimental Frequencies for *p*-Xylene

	p-xylene		[2.2]paracyclophane, **1**, calcd[b]				
	exptl	calcd	A	B$_1$	B$_2$	B$_3$	comments
				In−Plane Modes			
tangential[a]							
C−X bend							
9b	386	389	310	360			
15	292	288				300	
C−H bend							
3	1313	1310	1314	1316			
9a	1183	1180	1172	1171			for **1**, A mixed with 7a
18b	1100	1115			1170	1152 1085	B$_3$ mixed with CH$_2$ twist
18a	1248	1206			1184	1185	1248 assigned as 13 in ref 1
C−C stretch							
14	1324	1296			1291	1299	mixed with CH$_2$ twist
19b	1421	1408			1409	1415	
19a	1529	1516			1504	1504	
8b	1581	1577	1560	1564			
8a	1618	1620	1605	1603			
radial							
C−X stretch							
7a	1205	1194	1180	1176			A mixed with 9a for **1** mixed with CbCb stretch; 671 assigned as 12 in ref 1
20a	671	708			661		
C−H stretch							
2	3054	3063	3060	3058			
7b	3030	3044	3038	3071			
13	3095	3043			3040	3038	
20b	3017	3060			3054	3057	
skeletal							
6a	459	467	467	527			for **1**, B$_1$ mixed with 16b
6b	645	640	628	633			
12	1024	1009			1006	1003	1024 assigned 18a in ref 1
1	829	814	766				*p*-xylene mixed with 7a A, **1**, mixed with 17b & 16b
				Out-of-Plane			
C−X wagging							
10b	313	309				540	
11	170	137					not obvious in any one mode of **1**
C−H wagging							
5	934	925			924	931	
17b	795	786					for **1** mixed in 7 modes
10a	810	825			782	813	for **1** B$_3$ mixed with CH$_2$ rock
17a	962	934	928	937			
skeletal							
4	702	696			718	714	for **1**, B$_2$ mixed with CrCbCb bend and CbCb stretch
16a	410	421	438	457			
16b	483	501		320			though predominate at 320 for **1**, mixes in 8 modes

[a] *p*-Xylene experimental frequencies from ref 64. Mode descriptions are based on ref 64 and Varsányi, G.; Szöke, S. *Vibrational Spectra of Benzene Derivatives*; Academic: New York, 1969. [b] B3LYP/4-31G(d) used for determining calculated frequencies for *p*-xylene and **1**. Raw frequencies > 550 cm^{-1} are scaled by 0.963 (ref 37), and those < 550 cm^{-1} are scaled by 1.0013 (ref 38).

for *p*-xylene. For *p*-xylene we reassign the band near 1020 cm^{-1} from aromatic CH bend W18a to aromatic ring bend W12, the mode near 1240 cm^{-1} from $C-C^{Me}$ (CrCb for **1**) antisymmetric stretch to W18a mixed with a small contribution from the stretch, and finally, the mode near 670 cm^{-1} from W12 to $C-C^{Me}$ antisymmetric stretch, W20a. While these three Wilson modes exhibit some similarities to one another, the calculated normal modes indicate greater resemblance to the new assignments than to the old ones. (The diagrams for these modes of *p*-xylene are included in the Supporting Information, Figure 1SI, along with a table of the complete assignments, Table 1SI.) The calculated normal modes and frequencies for these three modes of **1** agree extremely well with these new assignments.

In contrast to *p*-xylene, in **1** the Cr−Cb symmetric stretch mode (W7a), which is in-phase with respect to the two decks, mixes with aromatic CH bend W9a, also in-phase with respect to the two decks. This results in two modes with nearly equal contributions of W7a and W9a, one in-phase and one out-of-phase with respect to each other. The vibrations of B$_1$ symmetry of W7a and W9a, each out-of-phase between decks, do not mix as strongly as their in-phase partners. The other major difference between modes of **1** and *p*-xylene in this region is mixing between benzene ring vibrations and CH$_2$ vibrations. A prime example is the in-phase (between decks) combination of CH bend W18b in **1** mixing with CH$_2$ twisting and thus splitting into two bands at 1152 and 1085 cm^{-1}. The out-of-phase combination in **1** of W18b is not significantly mixed and is calculated to occur at 1107 cm^{-1}, quite near W18b for *p*-xylene, 1100 cm^{-1} (exptl)[64] and 1115 cm^{-1} (calcd).

Overall the calculated normal modes for ‘in-plane’ vibrations of **1** are quite similar to those for *p*-xylene. Except for modes W6a, W1, W20a, and W18b, which mix with ‘out-of-plane’ vibrations, the calculated frequencies of **1** are within 21 cm^{-1} of the calculated frequencies for *p*-xylene, with the largest difference, of course, found where new mixing occurs. The calculated and experimental frequencies for the Wilson modes of *p*-xylene are shown in Table 5 and are compared with the calculated frequencies and assignments of **1**.

The various bends, twists, and wags of the methyl groups of *p*-xylene are much more difficult to compare with experiment, and there are no definitive assignments for these modes of **1**. Scudder and co-workers describe CH$_2$ scissoring as a “set of medium to strong i.r. bands occurring from 1440 to 1505 cm^{-1}, with the strongest at ... 1436 cm^{-1}".[15] Our calculations, however, show the strongest band is of B_2 symmetry at 1505 cm^{-1} and is assigned here to benzene ring mode W19a. The second strongest band near this region is a B_3 symmetric benzene ring mode W19b mixed with CH_2 twisting at 1415 cm^{-1}. The CH_2 scissoring modes are all calculated to be weak vibrations in IR. Our calculations are consistent with published spectra showing the strongest B_3 or B_1 band is ring stretching at 1415 cm^{-1} and the strongest B_2 in the vicinity is also ring stretching at 1505 cm^{-1}.[52]

While assignment of most of the 'in-plane' benzene ring vibrations of **1** based on nearby *p*-xylene modes is at least qualitatively accurate, several significant differences are revealed in our calculations. Combinations of translations, rotations, and 'in-plane' and 'out-of-plane' modes result in several normal modes that are now nominated as distinctive paracyclophane vibrations.

Conclusions

Unprecedented full geometry optimization with a split valence basis set and a method that includes electron correlation shows the equilibrium structure of [2.2]paracyclophane to be the twisted, D_2, conformation. The hybrid Hartree–Fock/density functional method B3LYP and 4-31G(d) basis set were used for geometry optimizations and vibrational analysis of both the D_2 and D_{2h} conformers. With a calculated twist angle of 3.9°, the D_2 conformer was both lower in energy and had no imaginary frequencies. The D_{2h} structure, on the other hand, produced one imaginary frequency, the paracyclophane twist mode. The calculated geometry of [2.2]paracyclophane is in very good agreement with the structure determined by X-ray crystallography.

We present the first complete assignment of all 90 normal harmonic vibrations of [2.2]paracyclophane. Upon examination of the calculated normal modes and comparison with prior assignments for paracyclophanes and *p*-xylene, we have identified vibrations that can be termed cyclophane specific modes. These include normal modes below 400 cm^{-1} which are combinations of motions that would be relative translations or rotations for fragments of [2.2]paracyclophane. Additionally, in the fingerprint region strong IR bands observed near 625, 723, and 880 cm^{-1} can be attributed to "paracyclophane vibrations" by virtue of substantial contributions to the normal modes from $C_{ring}C_{bridge}C_{bridge}$ (CrCbCb) bending and, to a lesser degree, CbCb stretching. The designation of paracyclophane-specific vibration should also be given to the strong IR band near 515 cm^{-1} since it is comprised of a forbidden combination of *p*-xylene in-plane a_g and out-of-plane b_u vibrations. The very intense Raman band near 790 cm^{-1} falls into both of these categories with contributions from 'in-plane' and 'out-of-plane' benzene vibrations and significant stretching of the CbCb bond. The remaining 'in-plane' vibrations are quite similar to calculated *p*-xylene modes in both frequency and mode description. Molecular vibrations that correspond to the boat deformation of benzene and symmetric wagging of the aromatic hydrogens are mixed extensively through the fingerprint region. Because these modes (for *p*-xylene or benzene) result in deformations already present in [2.2]paracyclophane, this mixing is not surprising.

Our calculated harmonic frequencies and relative intensities are in excellent overall agreement with the experimental IR spectrum. We have thus demonstrated the potential of hybrid Hartree–Fock/density functional theory as an electron-correlated method suitable and practical for characterizing even the large, highly strained, structurally and electronically unique parent of the [2.2]paracyclophane family.

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Supporting Information Available: Figure 1SI, selected normal modes calculated for *p*-xylene, and Table 1SI, calculated frequencies, symmetries, and assignments for *p*-xylene, (3 pages). See current masthead page for ordering and Internet access instructions.

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