Theoretical Study on the Molecular Distortions in [2.2]Paracyclophane and Cyclobutane

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Unrestricted geometry optimizations on [2.2]paracyclophane and cyclobutane at the MP2/6-31G(d) level led to significant ring distortions in agreement with experimental results. The MP2 method proved most successful in the study of the ring puckering of cyclobutane where various theoretical methods and basis sets were compared. Frequency calculations on [2.2]paracyclophane at the D_2 minimum and at the D_{2h} saddle point demonstrate the influence of the molecular twist on the vibrational spectra. The two distorted minima are separated by a C_{2h} symmetric barrier of 2.5 kJ/mol. Possible causes for the ring deformation in [2.2]paracyclophane are discussed.

1. Introduction

[2.2]Paracyclophane is often considered the key compound of the cyclophane family, partly because its synthesis in 1949 marked the beginning of cyclophane chemistry,[1] but also because this simple molecule exhibits all the typical cyclophane properties.[2,3] The most important of these features are the electronic interaction of the closely stacked π systems and the high amount of molecular strain, which manifests itself in the distortion of the benzene rings into a boat shape. This not only results in characteristic spectroscopic features but also explains unusual effects in the reactivity of [2.2]paracyclophane and its derivatives.[4−7]

Since its discovery [2.2]paracyclophane has stimulated considerable spectroscopic[8−16] and theoretical interest,[17−22] motivated by its unusual electronic structure. Until recently, most spectroscopic assignments were carried out on the basis of a D_{2h} molecular symmetry. This assumption, however, is not in agreement with the refined crystal structure reported by Hope et al.,[23] which suggests a twist of each aromatic ring of about 3° in opposite directions around the common normal, as illustrated in Figure 1. The concept of molecular distortion and the accompanying reduction of the molecular point group to D_2 is further supported by thermodynamic studies[24] and low-temperature absorption measurements on single crystals.[16] Despite the experimental evidence, spectroscopic assignments are often still based on D_{2h} symmetry. One reason for this ongoing use of D_{2h} symmetry is that geometry optimizations with semiempirical as well as ab initio methods predicted D_{2h} minima. Only very recently did a density functional calculation by Walden et al.[17] lead to a slightly twisted D_2 minimum, but the energy difference (0.35 cm^{-1}) between the two D_2 minima and the interconnecting D_{2h} saddle point is much too small to hold a vibrational zero-point level in the potential well. The only theoretical investigations that produce noticeable distortions are molecular mechanics calculations with MM2 and MM3 force fields by Allinger et al.[25] and by Ernst.[26]

The aim of this article is to resolve the debate on the molecular symmetry of [2.2]paracyclophane by presenting the results of highly correlated ab initio calculations that predict a distortion to D_2 symmetry, in accord with experimental data.

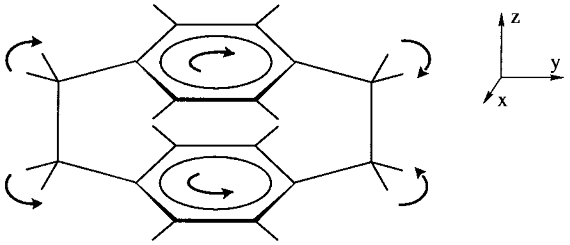

Figure 1. Schematic view of the distortion of [2.2]paracyclophane from D_{2h} symmetry.

To select a suitable quantum chemical method for the description of this phenomenon, we first studied the structure of the cyclobutane ring at various levels of theory. These studies were expected to provide a suitable guideline for the investigation of [2.2]paracyclophane since the conformational flexibility of this compound is partly due to the same factors as the ring puckering in cyclobutane. In particular, the sterical interactions of the adjacent methylene groups favor the staggered conformations in both molecules. The influence of the level of theory on the calculated amount of molecular distortion is discussed.

2. Computational Methods

All geometry optimizations and frequency calculations on cyclobutane and [2.2]paracyclophane were performed with the Gaussian 94[27] suite of programs. The AM1[28] and PM3[29] Hamiltonians were used for semiempirical calculations. As a representative density functional method Becke's hybrid exchange functional[30] was used together with the correlation functional derived by Lee, Yang, and Parr,[31] a combination denoted as B3LYP. Ab initio calculations were carried out at the restricted Hartree−Fock (RHF) and at the second-order Møller−Plesset (MP2) level. With the ab initio and the density functional computations, we applied various standard basis sets ranging from the minimal STO-3G basis to larger split valence basis sets, which include polarization and diffuse functions on all atoms.

The potential energy distributions (PED)[32] of the normal harmonic vibrations of [2.2]paracyclophane were determined with the locally developed program UNRAVEL,[33] in which the force field is solved in a set of internal coordinates.

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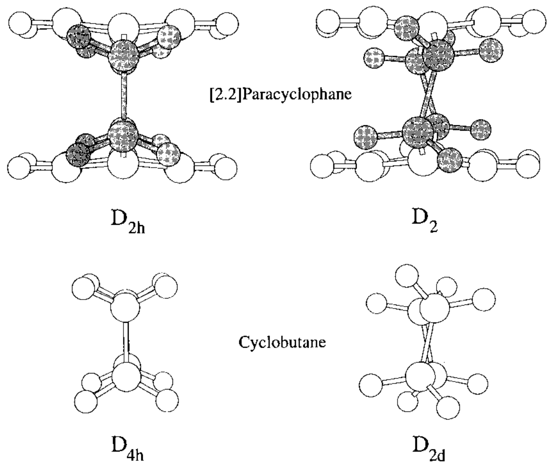

Figure 2. Eclipsed and distorted geometries of [2.2]paracyclophane and cyclobutane. Parts of the [2.2]paracyclophane structure are shaded to emphasize the similarity with cyclobutane.

3. Molecular Structure of Cyclobutane

Cyclobutane is an ideal test case to judge the suitability of quantum chemical methods for the description of ring distortions such as the twist in [2.2]paracyclophane. Figure 2 illustrates how closely the structures of cyclobutane and [2.2]paracyclophane are related. [2.2]Paracyclophane can be regarded as an extended cyclobutane where benzene units are inserted into two opposite aliphatic bonds. The conformational flexibility of the [2.2]paracyclophane super-ring strongly resembles the ring puckering motion in cyclobutane because the benzene units are relatively rigid and merely act as a spacer between the two halves of cyclobutane.

Cyclobutane has long been known to possess a puckered, D_{2d} symmetric ground-state structure.[34−36] Because of its small size this molecule has been accessible to a variety of quantum chemical approaches.[37−39,34] The twisting of the four-membered ring is caused by a relief of Pitzer strain. All ring hydrogen atoms are slightly staggered in the D_{2d} structure, as opposed to a totally eclipsed conformation in the planar, D_{4h} symmetric ring.

Owing to the small size of cyclobutane and the small number of normal harmonic vibrations, the ring puckering angle[40] and the torsional barrier could accurately be determined by an analysis of the gas-phase IR and Raman spectra.[34] The CCCC torsional angle τ was found to be $21 \pm 1°$ at the equilibrium geometry. The energy difference between the D_{4h} and the D_{2d} structures was determined as 513 cm^{-1}.

As a comparative study, we optimized the geometry of cyclobutane with both D_{4h} and D_{2d} symmetry restrictions with various quantum chemical methods and a number of different basis sets. Frequency calculations were used to verify the identification of these stationary points as local minima or transition states. Table 1 summarizes the resulting torsional angles τ at the equilibrium structures, the energy differences ΔE between the two stationary points of different symmetry, and the (mostly imaginary) frequencies ν of the twist motion at the D_{4h} geometry.

From a comparison of the experimentally determined torsional angle and barrier height with the theoretical values it is seen that the quality of the theoretical description depends critically on the choice of the quantum chemical method and the basis set. Neither of the two semiempirical methods AM1 and PM3 is capable of reproducing the ring puckering of cyclobutane. In both calculations the minimum geometry has D_{4h} symmetry and the real ring puckering frequencies are close to 200 cm^{-1}.

TABLE 1: Properties of Cyclobutane Determined with Different Methods

method	basis set	τ (deg)[a]	ΔE (cm^{-1})[b]	ν (cm^{-1})[c]	$E(D_{2d})$ (hartrees)[e]
AM1		0	0	210	
PM3		0	0	194	
RHF	STO-3G	5.7	3	41i	−154.273903
	4-31G	15.2	138	111i	−155.866811
	6-31G	15.3	140	112i	−156.030803
	4-31G(d)	18.1	311	138i	−155.942836
	6-31G(d)	18.2	318	139i	−156.097200
	6-31G(d,p)	18.4	339	142i	−156.109730
B3LYP	STO-3G	6.9	8	52i	−155.348991
	4-31G	15.3	132	115i	−157.009235
	6-31G	15.6	142	116i	−157.173230
	4-31G(d)	18.1	279	137i	−157.061436
	6-31G(d)	18.2	289	138i	−157.213151
	6-31G(d,p)	18.4	302	139i	−157.224448
	6-31G(2d,p)	18.1	277	132i	−157.224259
	6-31G(d,2p)	18.1	284	134i	−157.226224
	6-31++G(d,p)	18.3	301	136i	−157.229190
	cc-pVDZ	17.9	231	122i	−157.216395
MP2	STO-3G	10.5	30	65i	−154.482523
	4-31G	19.9	625	183i	−156.231012
	6-31G	20.2	721	198i	−156.392988
	4-31G(d)	21.4	740	183i	−156.464055
	6-31G(d)	21.6	792	189i	−156.617991
	6-31G(d,p)	22.3	891	195i	−156.682787
exptl[d]		21 ± 1	513 ± 2		

[a] CCCC torsional angle of cyclobutane. [b] Energy differences between the D_{4h} and the D_{2d} structures. [c] Frequencies ν of the ring twisting vibration at the D_{4h} stationary point. [d] Taken from ref 34. [e] Total energies at the D_{2d} minimum structures.

The Hartree−Fock, density functional B3LYP, and MP2 methods all produce distorted geometries, even with minimal basis sets. The HF and B3LYP results are generally very similar. Both methods underestimate the torsional angle and the energy difference ΔE. The torsional angles obtained at the MP2 level of theory are in good agreement with the experimentally determined value. The minimum geometries are much better than those obtained at the B3LYP and HF levels with the same basis sets. The torsional barrier, however, is generally overestimated with MP2 by about as much as the other methods underestimate it.

From the results of all three first principles methods, it can be seen that it is crucial to use at least moderately sized split valence basis sets to reproduce the ring puckering in cyclobutane. The inclusion of polarization functions on carbon atoms (d functions) causes an increase of the calculated twist angle, thus approaching the experimental value. The addition of polarization functions on hydrogen atoms (p functions) in the 6-31G(d,p) basis sets yields the largest and best torsional angles found with the HF and B3LYP methods in this study. Further enlargement of the basis set by inclusion of additional polarization or diffuse functions at the B3LYP level results in a slight decrease of the puckering amplitude.

The MP2 results are less sensitive to basis set changes than the other methods. With basis sets larger than 6-31G the MP2 computed twist angle becomes slightly larger than the experimental value but the differences are of the order of the experimental uncertainty. A more serious deficit of the MP2 calculations with larger basis sets is an inreasing overestimation of the barrier height. This could be due to an intramolecular basis set superposition error, which occurs because the positions of the basis functions change with the molecular geometry. This effect generally leads to overestimated inversion barriers.[41]

The investigation of cyclobutane with different quantum chemical methods seems to indicate that MP2 is the most

TABLE 2: Theoretical and Experimental Geometry Parameters of Cyclobutane

point group, deg of freedom	MP2 (6-31G(d)) D_{4h} 3	MP2 (6-31G(d)) D_{2d} 6	exptl D_{2d}
bond lengths (Å)			
CC	1.5502	1.5450	1.552[a]
CH_{eq}	1.0934	1.0939	1.093[a]
CH_{ax}		1.0946	1.093[a]
bond angles (deg)			
CCC	90	87.91	n.g.[b]
HCH	107.84	108.75	106.4[a]
torsional angles (deg)			
CCCC (τ)	0	21.64	21[c]
H_{ax} CCH_{eq}	0	31.39	n.g.[b]
ring puckering angle (deg)			
ρ	0	30.79	30[c]

[a] From ref 34. [b] Not given in the cited publications. [c] From ref 42.

suitable method for the description of distortion effects in strained ring systems. It produces the best geometries and the calculated barriers are reasonable estimates. To facilitate a comparison of the predicted stucture parameters of [2.2]paracyclophane and cyclobutane and of the effect of the distortion on these parameters, Table 2 summarizes the parameters obtained for the two stationary points of cyclobutane at the MP2/6-31G(d) level. The bond lengths and bond angles of the D_{2d} symmetric minimum geometry are in good agreement with the data available from a gas-phase electron diffraction study.[42]

4. Molecular Structure of [2.2]Paracyclophane

The ring distortion of [2.2]paracyclophane that was suggested by several experimental groups[9,10,16,23,24] is at least in part caused by the same factors as the ring puckering in cyclobutane: The hydrogen atoms of the ethano bridges prefer a staggered conformation, which can be approached by a twist of the cyclophane super-ring, and consequently a symmetry reduction to D_2. As the driving force of this twist is similar in [2.2]paracyclophane and cyclobutane, we expect that calculations on [2.2]paracyclophane at the MP2/6-31G(d) level of theory are of the same quality as the results we obtained for cyclobutane with this method. If the interaction of the two benzene units has an additional influence on the super-ring distortion, this effect should also be well accounted for in an MP2 calculation, because the MP2 method proved successful in studies of interactions in the benzene dimer.[43]

We performed a restricted geometry optimization of [2.2]paracyclophane in D_{2h} symmetry and a full, unrestricted optimization which converged into a D_2 symmetric structure. The structure parameters at these two stationary points are compiled in Table 3. The available parameters from the refined X-ray structure and the B3LYP optimized structure by Walden et al.[17] are shown for comparison. Figure 3 shows two perspectives of the MP2/6-31G(d) minimum geometry and illustrates the numbering of atoms used in Table 3.

The minimum geometry exhibits a considerable distortion of the [2.2]paracyclophane super-ring, in accord with experimental

TABLE 3: Theoretical and Experimental Geometry Parameters of [2.2]Paracyclophane

point group, deg of freedom	MP2 (6-31G(d)) D_{2h} 13	MP2 (6-31G(d)) D_2 24	exptl[b] D_2 24	B3LYP[d] (4-31G(d)) D_2 24
bond lengths[a] (Å)				
$C_7C_{7'}$	1.5965	1.5856	1.593	1.610
C_1C_2	1.4025	1.4033	1.386	1.400
C_3C_4		1.4017	1.385[c]	1.399
C_2C_3	1.3949	1.3952	1.387	1.391
C_1C_7	1.5095	1.5080	1.511	1.512
C_2H_9	1.0898	1.0896	1.00	
C_3H_{10}		1.0900		
C_7H_{13}	1.0961	1.0970	1.02	
C_7H_{14}		1.0962	1.08	
bond angles[a] (deg)				
$C_1C_7H_{13}$	110.05	112.10	112	110.57
$C_1C_7H_{14}$		108.72	107	109.93
$C_1C_2C_3$	120.62	120.95	120.7	120.80
$C_2C_3C_4$		120.25	120.7[c]	120.66
$C_3C_2H_9$	119.40	119.21	118.8[c]	
$C_2C_3H_{10}$		119.38		
$C_1C_7C_{7'}$	112.68	112.00	112.6[c]	113.56
$C_2C_1C_7$	120.70	120.13	120.9	120.74
$C_6C_1C_7$		121.13	120.9[c]	121.08
$C_2C_1C_6$	117.32	117.25	117.0	116.87
$H_{13}C_7H_{14}$	106.80	106.86	109	106.76
torsional angles[a] (deg)				
$C_1C_7C_{7'}C_{1'}$	**0**	**21.82**	**16.1**[c]	**3.9**
$H_{13}C_7C_{7'}H_{13'}$	0	25.85	19.4[c]	
$C_1C_7C_{7'}H_{13'}$	± 122.14	145.97	139.0[c]	
$C_1C_7C_{7'}H_{14'}$		−98.29	−103.5[c]	
$C_1C_2C_3C_4$	0	−0.84	0[c]	
$C_2C_3C_4C_5$	13.61	14.50	14.6[c]	
$C_4C_3C_2H_9$	171.98	170.90	169.7[c]	
$C_1C_2C_3H_{10}$		188.30		
ring twist[a] (deg)				
β	**0**	**4.0**	**3.2**	
ring separation[a] (Å)				
$C_1C_{1'}$	2.7580	2.7664	2.782[c]	2.820
$C_2C_{2'}$	3.0533	3.0727	3.096[c]	3.138

[a] For atom numbering and twist angle definition, see Figure 3. [b] From ref 23. [c] These values were not explicitly given in ref 23, but were recalculated from the available position parameters. [d] From ref 17.

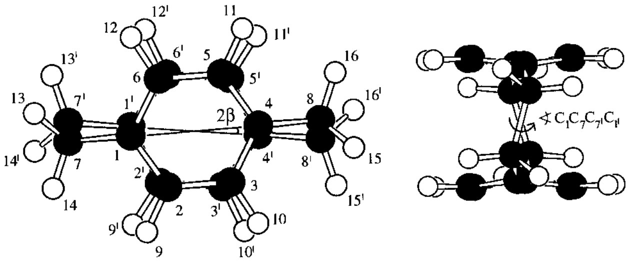

Figure 3. Two views of the MP2/6-31G(d) minimum geometry of [2.2]paracyclophane.

findings. The amount of distortion at the MP2/6-31G(d) minimum is much higher than the twist in the B3LYP/4-31G(d) structure.[17] The $C_1C_7C_{7'}C_{1'}$ torsional angle predicted in our MP2 calculation amounts to 21.82°. In their report on the refined cystal structure Hope et al.[23] use the twist angle of each ring about the common normal to quantify the amount of ring distortion (angle β in Figure 3). As we already pointed out in ref 44, this angle differs substantially from the torsional angle $C_1C_7C_{7'}C_{1'}$ (see Table 3). The agreement of the MP2 geometry parameters with the X-ray structure is very good. The fact that our calculated $C_1C_7C_{7'}C_{1'}$ torsional angle is somewhat larger than the experimental value could be due to difficulties in distinguishing between the distortion of the equilibrium structure and the average thermal distortion at room temperature in the experiment. The results obtained for cyclobutane with a series of different basis sets indicate that the deviation from the experimental estimate is probably not due to the small basis set size.

Apart from the $C_1C_7C_{7'}C_{1'}$ torsional angle, there are several other parameters that undergo notable changes when moving from the D_{2h} symmetric saddle point to the D_2 minimum. Of particular interest are the bond angles $C_1C_7H_{13/14}$ and the torsional angles $C_1C_7C_{7'}H_{13'/14}$. The theoretical values for these parameters are in good agreement with the experimentally observed splittings. The changes in these angles cause a further decrease in the steric interaction of the bridge hydrogen atoms. Accordingly, the $H_{13}C_7C_{7'}H_{13'}$ torsional angle is larger (25.85°) than the torsional angle of the carbon frame (21.82°). This effect is, however, less pronounced than it is in cyclobutane where the axial and equatorial hydrogen atoms form a torsional angle as high as 31.39°.

In contrast to the ethano groups, the benzene subunits are very rigid and none of the internal parameters changes significantly. The inter-ring distance, however, is affected by the twist. In Table 3 two values are given for the ring separation because of the boatlike deformation of the benzene rings. Contrary to the assumptions made by Hope et al.,[23] we found that the distance between the two aromatic rings is increased by the molecular deformation, even though the ethano bridge bonds and the bridge−ring bonds are both shortened. The reason is that the rings also become slightly staggered in the twisted conformation. Therefore the projections of the bridge−ring bonds onto the z axis are enlarged in the D_2 structure.

The $C_1C_7C_{7'}C_{1'}$ torsional angle of [2.2]paracyclophane (21.82°) and the CCCC torsional angle of cyclobutane (21.64°) that we obtained at the MP2/6-31G(d) level are surprisingly similar. This indicates that in [2.2]paracyclophane the steric interaction of the bridge hydrogen atoms is not the only reason for the twist, since there are only half as many closely interacting CH_2 pairs in [2.2]paracyclophane as in cyclobutane. Therefore, the twist should be lower in [2.2]paracyclophane if the hydrogen interaction was the only reason for the deformation. There are two additional factors that probably contribute to the deformation: first, the increase in the inter-ring distance and, second, the slightly staggered conformation of the atoms in the aromatic rings in the twisted structure.

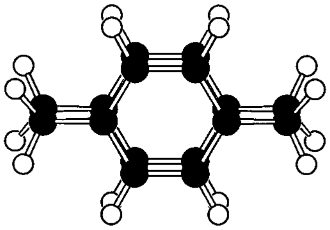

Figure 4. C_{2h} symmetric first-order saddle point of [2.2]paracyclophane viewed in the direction of the ring normal.

5. Vibrational Analyses of [2.2]Paracyclophane

All frequency calculations on stationary points of [2.2]paracyclophane were carried out at the MP2/6-31G level of theory, because the 6-31G(d) basis set was not practicable for force field calculations of this relatively large molecule with the available computing facilities. For the frequency analyses the stationary points were reoptimized with the 6-31G basis set. The resulting geometries deviate very little from the corresponding MP2/6-31G(d) structures. In particular, the $C_1C_7C_{7'}C_{1'}$ torsional angle is only 0.4° higher than at the MP2/6-31G(d) minimum.

A frequency calculation for the optimized, D_2 symmetric structure verified that this structure is a true minimum geometry. For the D_{2h} structure the frequency analysis revealed two negative eigenvalues, leading to two imaginary frequencies. This was surprising since in earlier discussions the D_{2h} symmetric stationary point had always been considered a first-order saddle point with one imaginary frequency that corresponds to the twist motion.[9,17] In our calculation we find a frequency of 80 i cm^{-1} for this twisting motion. The second imaginary frequency has a value of only 37 i cm^{-1} and belongs to a B_2 symmetric benzene rocking motion.

The discovery of the second imaginary frequency raised the question whether the corresponding motion leads to a second minimum energy conformation or to a first-order saddle point. We performed an optimization of a geometry displaced along this B_2 mode, with C_{2h} symmetry restriction. A frequency analysis revealed that the resulting geometry is a first-order saddle point with an imaginary bridge-twisting frequency of 40 i cm^{-1}. Therefore, no further minimum structures are expected to occur in this region of the potential energy surface. The optimized geometry of the C_{2h} symmetric saddle point is shown in Figure 4. In this structure the aromatic rings are displaced by 0.3 Å.

The lowest barrier to interconversion of the two equivalent, twisted D_2 minima is the C_{2h} saddle point, which is 2.53 kJ/mol (211 cm^{-1}) higher in enery than those of the minimum structures. The D_{2h} symmetric second-order saddle point lies only slightly higher at 2.73 kJ/mol (228 cm^{-1}) above the energy minimum. These values are much larger than the barrier height of 0.35 cm^{-1} found in the B3LYP calculation.[17] Since for cyclobutane the MP2/6-31G barrier is about 40% above the experimental value, it is likely that the barrier in [2.2]paracyclophane is also somewhat overestimated by our calculations. However, the order of magnitude should be correct, and the zero-point energy level for the twisting vibration is well below the barrier height (freqencies given in Table 4) even if this barrier is only half as high as calculated. This implies that the existence of the two equivalent distorted minima is not merely

TABLE 4: Theoretical (MP2/6-31G) and Experimental Vibrational Frequencies of [2.2]Paracyclophane

MP2 in D_{2h}		MP2 in D_2			exptl	MP2 in D_{2h}		MP2 in D_2			exptl
freqs[a]	int[b]	freqs[a]	int[b]	PED[c]	freqs[a]	freqs[a]	int[b]	freqs[a]	int[b]	PED[c]	freqs[a]
A Modes											
3048	0.00	3048	0.00	ν(C_rH) 99	3044	**955**	0.00	**989**	0.00	r(C_bH_2) 72	
3021	0.00	3021	0.00	ν(C_rH) 99		863	0.00	876	0.00	ν(C_bC_b) 66	905
2964	0.00	2964	0.00	ν(C_bH) 99		781	0.00	792	0.00	w(C_rH) 85	790
2931	0.00	2928	0.00	ν(C_bH) 100	2937	780	0.00	783	0.00	δ(1,4) 25, ν(C_rC_r) 21	
1562	0.00	1560	0.00	ν(C_rC_r) 60, b(C_rH) 21	1594	741	0.00	750	0.00	w(C_rH) 72	
1524	0.00	1524	0.00	ν(C_rC_r) 65		624	0.00	624	0.00	δ(2,5) 80	637
1497	0.00	1497	0.00	sc(C_bH_2) 90		534	0.00	534	0.00	τ(boat) 58, w(C_rC_b) 26	568
1314	0.00	1327	0.00	b(C_rH) 58, tw(C_bH_2)20	1323	447	0.00	449	0.00	δ(1,4) 70	465
1272	0.00	1277	0.00	w(C_bH_2) 49, b(C_rH) 27		387	0.00	396	0.00	τ(twist) 50, w(C_rH) 25	
1222	0.00	1214	0.00	tw(C_bH_2) 50, w(C_bH_2) 27		**283**	0.00	**320**	0.00	b(C_rC_b) 38, τ(twist) 22	
1187	0.00	1188	0.00	b(C_rH) 77, ν(C_rC_r) 22	1180	231	0.00	227	0.00	w(C_rC_b) 50, τ(twist) 39	243
1164	0.00	1162	0.00	ν(C_rC_b) 45, ν(C_rC_r) 28		**73 i**	0.00	**85**	0.00	τ(s-ring) 69, w(C_rC_b) 21	
B_1 Modes											
3045	4.40	3045	4.08	ν(C_rH) 99	3037	1160	0.00	1148	0.17	tw(C_bH_2) 62	
3024	0.00	3024	0.08	ν(C_rH) 99		**836**	6.09	**869**	9.19	r(C_bH_2) 29, ν(C_rC_r) 20	896
2988	0.00	2984	4.31	ν(C_bH) 99		802	0.00	805	0.04	w(C_rH) 84	
2917	38.38	2918	26.87	ν(C_bH) 100	2927	787	0.00	783	3.71	r(C_bH_2) 29, ν(C_rC_r) 25	
1560	7.46	1558	7.91	ν(C_rC_r) 60, b(C_rH) 21	1596	756	63.49	752	62.47	w(C_rH) 61	
1528	0.00	1528	0.01	ν(C_rC_r) 67		631	0.00	631	2.00	δ(2,5) 75	624
1476	1.18	1486	0.66	sc(C_bH_2) 95	1440	612	44.95	598	40.09	w(C_rH) 40	541
1328	1.49	1340	0.98	w(C_bH_2) 81	1324	478	20.87	487	20.62	δ(1,4) 39, w(C_rC_b) 23, τ(boat) 23	510
1318	0.00	1315	0.06	b(C_rH) 72		416	0.00	419	0.02	τ(twist) 44, w(C_rH) 22	
1184	1.55	1185	1.49	b(C_rH) 78, ν(C_rC_r) 20	1180	343	0.00	350	0.27	b(C_rC_b) 33, τ(twist) 33	
1168	2.02	1171	1.37	ν(C_rC_r) 35, ν(C_rC_b) 35		292	0.01	288	0.16	τ(boat) 40, w(C_rC_b) 30	
B_2 Modes											
3040	0.00	3040	0.00	ν(C_rH) 99		1109	0.00	1112	0.82	b(C_rH) 51, ν(C_rC_r) 28	
3024	39.99	3024	39.33	ν(C_rH) 99	3017	1002	0.16	1002	0.17	δ(1,3,5) 55,m, ν(C_rC_r) 32	
2964	0.00	2964	20.14	ν(C_bH) 99		**919**	0.00	**954**	2.04	r(C_bH_2) 60, ν(C_rC_r) 24	937
2931	165.27	2927	144.35	ν(C_bH) 100	2932	859	1.21	874	0.90	ν(C_bC_b) 69	890
1497	4.46	1498	2.64	sc(C_bH_2) 94	1505	809	29.72	811	32.29	w(C_rH) 93	
1479	13.13	1479	14.42	b(C_rH) 55, ν(C_rC_r) 32	1445	730	0.00	732	0.00	w(C_rH) 88	721
1384	0.00	1386	0.68	b(C_rH) 38, ν(C_rC_r) 35		660	3.98	661	2.94	ν(C_rC_b) 50	
1337	0.00	1340	0.57	ν(C_rC_r) 78		**519**	5.75	**544**	6.03	τ(chair) 77	
1270	10.09	1278	0.49	w(C_bH_2) 53, ν(C_rC_r) 24		364	0.78	362	0.75	w(C_rC_b) 88	384
1220	0.00	1220	5.76	tw(C_bH_2) 36	1230	**185**	0.00	**249**	0.13	b(C_rC_b) 49, r(ring) 24	
1190	0.04	1182	0.70	ν(C_rC_b) 29		**34 i**	0.00	**70**	0.03	r(ring) 90	
B_3 Modes											
3043	88.98	3043	86.52	ν(C_rH) 99	3070	1075	3.49	1074	3.73	ν(C_rC_r) 42, b(C_rH) 25, tw(C_bH_2) 24	1089
3022	0.00	3022	0.07	ν(C_rH) 99		999	0.00	1000	0.00	δ(1,3,5) 55, ν(C_rC_r) 31	
2988	57.95	2985	51.90	ν(C_bH) 99	2956	**796**	0.00	**838**	0.11	r(C_bH_2) 44, δ(s-ring) 26	855
2917	0.00	2918	9.54	ν(C_bH) 100		781	0.00	801	0.04	w(C_rH) 88	
1484	0.00	1492	5.75	sc(C_bH_2) 76		**891**	1.51	**759**	6.28	w(C_rH) 81	
1470	0.00	1475	1.53	b(C_rH) 43, ν(C_rC_r) 25, sc(C_bH_2) 20		**748**	3.80	**722**	0.65	r(C_bH_2) 36	
1393	14.51	1391	13.03	b(C_rH) 36, ν(C_rC_r) 35	1415	**564**	0.00	**587**	0.01	τ(chair) 36	
1337	0.29	1341	0.39	ν(C_rC_r) 51, w(C_bH_2) 33		**440**	0.00	**464**	0.00	w(C_rC_b) 56, τ(chair) 36	
1328	0.00	1332	0.00	ν(C_rC_r) 45, w(C_bH_2) 34		290	0.16	294	0.15	b(C_rC_b) 71	
1195	0.00	1195	0.03	ν(C_rC_b) 32, b(C_rH) 23, δ(1,3,5) 21		156	0.26	156	0.29	w(C_rC_b) 64, r(ring) 27	
1167	2.16	1163	2.00	tw(C_bH_2) 52, b(C_rH) 27	1170	137	0.00	135	0.12	w(C_rC_b) 80	

[a] Scaled (factor 0.96) frequencies in cm^{-1}. [b] In kM/mol. [c] Potential energy distributions normalized to a total of 100. Coordinates with PED values greater than 20 are listed. Internal coordinate description: ν = stretch; b = pseudo-in-plane bend; sc = scissor; r = rock; w = wag; tw = twist; δ = ring deformation; τ = ring torsion; s-ring = super-ring; subscript b = bridge; subscript r = ring.

a topological property of the potential energy surface. It really has experimental relevance because the vibrational ground state corresponds to a twisted, D_2 symmetric structure.

The results of the MP2/6-31G frequency analyses of [2.2]paracyclophane at the D_{2h} saddle point and at the D_2 symmetric minimum are collected in Table 4. The frequencies are scaled with a factor 0.96. This is the scaling factor optimized by DeFrees et al.[45] for MP2/6-31G(d) calculations. The factors recommended in the literature for scaling MP2/6-31G(d) frequencies range from 0.94 to 0.96.[45,46] For our MP2/6-31G frequency calculations we used the value 0.96, since it produces the best agreement with experimental frequencies. In Table 4 we also show the assignment of some of the calculated frequencies to the IR and Raman bands observed in the polarized crystal spectra by Schettino et al..[14] The scaled frequencies agree well with the experimental band positions, and the vibrational assignment is mostly in accordance with the results of the B3LYP study by Walden et al.[17] For the equilibrium structure the calculated potential energy distributions (PED) provide a quantitative measure of the contribution of selected internal coordinates to the normal vibrations.

One consequence of the symmetry reduction is that several modes that are symmetry-forbidden in D_{2h} gain intensity (see Table 4). Thirteen of these modes have an IR intensity of more than 0.25 kM/mol at the distorted equilibrium geometry. In constrast, the B3LYP frequency analysis of Walden et al.[17] produced only six modes that gained this much intensity. This is due to the much smaller distortion in the latter calculation.

The 13 normal modes that change in frequency by more than 20 cm^{-1} are set in bold font in Table 4. Only one of these modes shows a noticeable intensity gain due to the symmetry reduction. The two imaginary frequencies of the D_{2h} saddle point become real at the local minimum and attain values of 85 cm^{-1} for the twist motion and 70 cm^{-1} for the benzene rocking motion. The twist motion was assigned to a 72 cm^{-1} progression in the jet fluorescence excitation spectrum by Ron et al.[10] Walden et al.[17] questioned this assignment because their calculated twist frequency was only 22 cm^{-1}, and their B_2 ring rocking frequency of 78 cm^{-1} agreed much better with the observed progression. The latter assignment neglects the fact that the polarized spectra of Ron et al.[15,10] revealed the progression forming mode as totally symmetric. Our MP2 results support the assignment of Ron et al. The calculated twisting frequency of 85 cm^{-1} is close to the observed value of 72 cm^{-1}. The remaining deviation may in part result from the strong anharmonicity of the double minimum potential and from a possible frequency shift between ground and excited-state vibrations.

Only two other modes that undergo major frequency changes with the twist can be assigned to experimental bands. One is the B_3 symmetric CH_2 rocking and super-ring deformation mode calculated at 838 cm^{-1} in D_2 and assigned to a band observed at 855 cm^{-1}. Compared with the D_{2h} value of 796 cm^{-1}, the agreement between experimental and theoretical value is clearly improved. The other twist sensitive mode that could be assigned to an IR band is the B_2 symmetric CH_2 rocking mode calculated at 954 cm^{-1}. However, the intensity calculated for this vibration is much weaker than the intensity of the band at 937 cm^{-1} in the IR spectrum, and the assignment is not entirely certain. More detailed experimental information on the weaker bands is necessary to analyze the influence of the symmetry distortion on both frequencies and band intensities more closely. In particular, highly resolved IR, Raman, or fluorescence measurements of the low-frequency transitions are needed.

6. Conclusion

The symmetry lowering in cyclobutane from D_{4h} to D_{2d} could be described with restricted Hartree–Fock, density functional (B3LYP), and second-order Møller Plesset calculations. The amount of distortion depends critically on the choice of the method and on the basis set. At the MP2/6-31G(d) level, very good agreement is achieved between theoretical and experimental geometries.

For [2.2]paracyclophane the MP2/6-31G(d) calculations predict a D_2 structure with a CCCC torsional angle of 21.8° about the ethano bond. This is the first calculated geometry that exhibits a distortion comparable to the experimental observations.[23] To a large extent, the distortion is caused by the same factors as the ring puckering of cyclobutane. In both molecules the ethano moieties prefer a staggered conformation of the hydrogen atoms, which can be achieved by a twist of the rings.

Frequency calculations at the MP2/6-31G level show that at least the zero-point level of the twisting vibration fits into the potential wells at the D_2 minima. The D_{2h} symmetric stationary point turned out to be a second-order saddle point with imaginary frequencies for the molecular twisting and the benzene rocking vibration. A C_{2h} symmetric first-order saddle point lies 2.53 kJ/mol (211 cm^{-1}) above the energetic minima and forms the lowest barrier for interconversion of the two equivalent D_2 minima.

Comparison of the scaled harmonic frequencies calculated at the D_2 minimum and at the D_{2h} saddle point shows that the molecular distortion has a pronounced influence on the frequencies of a number of weak transitions, most of which have not yet been observed experimentally.

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