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COMMENTS

Comment on “Distinctive Normal Harmonic Vibrations of [2.2]Paracyclophane”

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In this journal Walden et al.[1] recently reported a vibrational analysis of [2.2]paracyclophane on the basis of density functional (B3LYP/4-31G(d)) calculations. In the course of this study the authors performed an unrestricted geometry optimization and found a local minimum with D_2 symmetry. In this conformation the aromatic rings are slightly twisted and the ethano hydrogen atoms are not fully eclipsed. This kind of deviation from D_{2h} symmetry had been suggested by experimentalists[2−5] but was not confirmed in earlier theoretical investigations.[2,6]

Walden et al. claim that the amount of symmetry distortion found in their calculations compares excellently with the result of a crystal structure analysis by Hope et al.[3] Unfortunately, in this comparison Walden et al. do not use the same definition of the twist angle as the experimentalists. Hope et al. express the extent of distortion in terms of the twist of each ring about the common normal, which was found to amount to 3.2°. This twist angle β is shown schematically in Figure 1. Walden et al. on the other hand discuss the molecular deformation on the basis of the torsional angle CrCbCbCr which has a value of 3.9° at the minimum found in their calculation. The direct comparison of these two angles is deceptive, because their values differ significantly at a given geometry. The differences become obvious in Table 1 where the available values of both angles are given for the X-ray structure[3] and for the B3LYP/4-31G(d) minimum obtained by Walden et al.[1] Table 1 shows that a comparison of the calculated twist angle CrCbCbCr of 3.9° with the corresponding angle in the X-ray structure of 16.1° is less favorable.

The second point to be addressed is the height of the barrier between the two degenerate D_2 conformers, i.e., the energy difference ΔE between the D_{2h} and D_2 structures. Walden et al. report a calculated energy difference of only 1×10^{-3} kcal/mol (0.35 cm^{-1}). With their calculated value of 22 cm^{-1} for the twisting frequency the D_2 minima are much too shallow to hold the corresponding zero-point energy level. It must be pointed out that in this case the ground state wave function still possesses D_{2h} symmetry and not D_2, as claimed by Walden et al. The predicted symmetry reduction of the potential minimum would have no observable relevance at all, and the conclusion that the results are in accord with the thermodynamic properties that suggest a “freezing” of the twist motion below 50 K[5] is deceptive. Thus, the geometry parameters of the twisted D_2 minima should not be compared to the experimental structure at all.

Even though the B3LYP results of Walden et al. are an improvement over previous RHF calculations,[2] in that the eclipsed D_{2h} structure is somewhat destabilized, the energy difference between the D_2 and D_{2h} structures is far below the numerical accuracy of the B3LYP method. Thus, the stabilization of the D_2 geometry could even be an integration grid artefact, similar to the false stationary points found in density functional calculations of the pseudorotation in tetrahydrofuran.[7] One possible reason for the inability of the B3LYP method to produce a distorted ground state wavefunction for [2.2]paracyclophane is that the correlation effects in noncovalently bonded systems are not fully accounted for. This suggests that non-Coulombic interactions of the aromatic rings could be one of the driving forces for the distortion, together with the tendency of the bridge hydrogen atoms to avoid an eclipsed conformation.

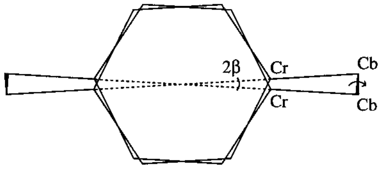

Figure 1. Schematic view of the twisted carbon skeleton of [2.2]-paracyclophane, the “half” twist angle β, and the torsional angle CrCbCbCr.

TABLE 1: Experimental and Calculated Twist Angles, Torsional Angles, Barrier Heights and Twisting Frequencies[a]

	exptl[2−4]	B3LYP[1]/4-31G(d)	MP2/6-31G
β [deg]	3.2		3.9
CrCbCbCr [deg]	16.1	3.9	22.2
ΔE [cm^{-1}]		0.35	228
ν (twist) [cm^{-1}]	33−72	22	90

[a] Experimental angles are taken from or calculated from values given in ref 3; different experimental twisting frequencies are found in refs 2 and 4.

In the past the MP2 method has proven successful in studies of interactions in the benzene dimer.[8] Therefore we performed calculations on the structure and vibrations of [2.2]paracyclophane at the MP2/6-31G level of theory, using the Gaussian 94 program suite.[9] The values in Table 1 demonstrate that these calculations yield a suitable description of the molecular distortion. In particular, the interconversion barrier is high enough for the D_2 potential minima to hold not only the zero-point level of the twisting vibration but also at least one excited vibrational level of this mode. Thus, our results are the first to produce a ground state with reduced symmetry and confirm the experimentally observed distortion to a D_2 symmetric structure. The angles for ethano torsion and ring twist compare well with experimental findings. The fact that our harmonic twist frequency is somewhat higher than all experimentally assigned frequencies is probably due to the strong anharmonicity of the double minimum potential.

References and Notes

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