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ON THE MOLECULAR STRUCTURE OF CYCLOHEPTADIENE[1,*]

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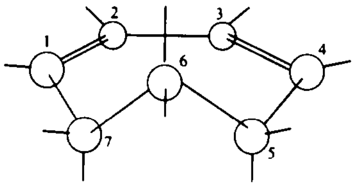
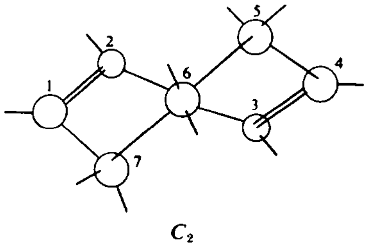
Abstract—Molecular mechanics calculations on cycloheptadiene indicate that the molecule has a structure which undergoes a wide pseudorotational motion between two C_1 forms, and a C_s form, and this structure is in equilibrium with the C_2 form. It is shown that this equilibrium mixture is consistent with all of the available experimental data.

Conflicting conclusions have been published concerning the conformation of 1,3-cycloheptadiene. From a gas phase electron diffraction investigation, Chiang and Bauer[2] reported that a C_s form fits the data better than any of a variety of other planar and non-planar structures, including a "boat-like" structure of C_2 symmetry. Presuming considerable bond angle strain in the C_s, estimated at about 7 kcal/mole, they suggested that the C_2 suffered at least an equivalent destabilization through loss of conjugation across the C_2—C_3 bond and through the non-bonded repulsion of a C_5 (and C_7) hydrogen with the π-orbital of C_1 (and C_4). In a molecular mechanical study of conjugated cyclic dienes, Favini and coworkers[3] found the C_2, with a 55° dihedral angle across the C_2—C_3 bond, to be the most stable conformation, being preferred over the C_s by 4·3 kcal/mole. Their method, however, suffers from a very limited test set of molecules and a rather simplified force field, considering only ring angle deformations, H · · · H non-bonded repulsions and ring carbon torsional strain. More recently, Crews,[4] studying the NMR coupling constants of the C_2 and C_3 protons, concluded that the C_2—C_3 bond was twisted about 20°, and the molecule therefore existed as the C_2 conformer. This assignment was based on a $J_{2,3}$ of 6·89 Hz for 1,3-cycloheptadiene which is midway between 5·5 Hz for a twisted C_{sp^2}—C_{sp^2} single bond and 8·4 Hz for a planar system.[5]

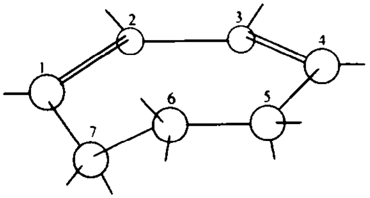


C_s



C_2

Hoping to resolve this problem we studied these two conformations of cycloheptadiene with the aid of a previously described and well-tested molecular mechanical model,[6] and found that they occupy local minima of essentially identical energy ($\Delta E = 0{\cdot}05$ kcal/mole). The C_s conformer (extremely shallow minima) is characterized by a methylene group 0·76 Å above the plane of the other 6 ring atoms, and the C_2 form by a 45° dihedral angle across the C_2—C_3 bond. From an examination of models it was also concluded that the molecule should undergo a rather facile pseudorotation resulting in an interconversion of these forms. Following this interconversion from the C_s conformer by rotating C_5 above the plane of the ring and C_7 below it, we find the C_s form can distort to a non-symmetrical form (C_1), characterized by the coplanarity of atoms C_2, C_3,



C_1

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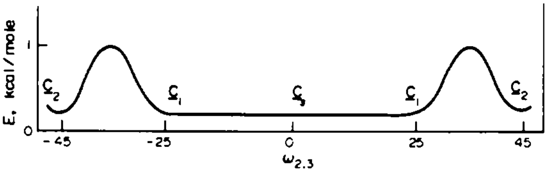
C_4, C_5 and C_6, with a ΔE of less than 0·02 kcal/mole and no barrier separating the two forms. The dihedral angle across the C_2—C_3 bond is 24·5°. A barrier of approximately 1 kcal/mole, caused by the ethane-type eclipsing between the C_5 and C_6 hydrogens and the propene-type eclipsing between the C_4 and C_5 hydrogens, then separates this nonsymmetrical form from the C_2 form. The potential energy diagram for this low energy pseudorotation is shown in the figure.



'Fig 1. Pseudorotation in 1,3-cycloheptadiene.

From this diagram one can see that the NMR data can be interpreted in terms of a pseudorotationally averaged C_2—C_3 dihedral angle rather than a single C_2 conformer of fixed geometry. This conclusion does not necessarily conflict with the diffraction data either since Chiang and Bauer considered only single conformations in constructing the theoretical radial distribution curves, selecting then the conformation which best fit the data. The possibility of conformer mixtures, or as we find, an almost unhindered pseudorotation, was not considered.

Details of our calculated structures are shown in Table 1, along with the diffraction results.

Table 1. Geometry of 1,3-cycloheptadiene

	Ref. 2	Calculated		
	(C_s)	C_s	C_1	C_2
1–2, 3–4	1·35±0·01	1·346	1·344, 1·346	1·344
2–3	1·48±0·01	1·469	1·472	1·480
1–7, 4–5	1·54±0·01	1·504	1·505, 1·506	1·510
5–6, 6–7	1·55±0·01	1·525	1·525, 1·526	1·527
1–2–3	129±2°	129·4°	126·3°, 128·8°	120·7°
2–1–7	129±2°	128·3°	123·8°, 130·1°	121·5°
1–7–6	119±2°	115·0°	110·1°, 118·8°	113·5°
5–6–7	119±2°	112·8°	111·5°	111·9°
1–2–3–4	0°	0°	24·5°	45·0°

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