

AB INITIO CALCULATIONS ON PLANAR AND BOAT CONFORMATIONS OF 1,4-CYCLOHEXADIENE

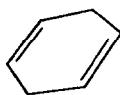
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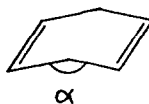
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The geometric structure of 1,4-cyclohexadiene has recently been studied by a number of methods, e.g., Raman and ir,<sup>1</sup> mmr,<sup>2</sup> electron diffraction,<sup>3,4</sup> and force field<sup>5</sup> calculations. Contradictory results have been obtained. In particular, the two studies using electron diffraction differ in that one suggests a planar conformation for 1,4-cyclohexadiene (1),<sup>3</sup> while according to the other, a boat conformation (2) (dihedral angle 159.3) is the most stable.<sup>4</sup>



1



2

angle between planes  
 $\alpha = 159.3$  (ref 4)

Conformational studies are often successfully performed using the *ab initio* method.<sup>6</sup> In this study the two suggested conformations 1 and 2 were subjected to *ab initio* total energy calculations. The calculations indicate that the planar conformation is about 7 kcal·mol<sup>-1</sup> more stable than the bent one.

Geometries as determined by electron diffraction for 1<sup>3</sup> and 2<sup>4</sup> were used, except that the same bond lengths were used in both calculations.<sup>7</sup>

A Gaussian basis set of seven s-type and three p-type functions contracted to four and two, respectively, was used for carbon.<sup>8</sup> The basis set for hydrogen was formed from four s-type primitive Gaussian functions contracted to two.<sup>9</sup> The calculations were performed with the computer program MOLECULE.<sup>10</sup>

Total energies for 1 and 2 were calculated to -231.5610 and -231.5491 a.u., respectively. This corresponds to 1 being 7.4 kcal·mol<sup>-1</sup> more stable than 2. The highest occupied  $\pi$ -level, formally the SS combination of the two olefinic  $\pi$ -orbitals, has about 0.95 eV higher energy in both conformations than the orbital represented by the SA combination. This is in excellent agreement with experimental results<sup>11</sup> (Table 2).

Table 1

Conformation	Angle ( $\alpha$ )	Total energy (a.u.)	$\Delta E_{SS-SA}^a$ (eV)
<u>1</u>	180	-231.5610	0.95
<u>2</u>	159.3	-231.5491	0.96

<sup>a</sup>Exp. value 1.0 eV, ref 11.

A comparison between ionization potentials and calculated valence orbital energies for 1 is given in Table 2. The difference between calculated and observed IP for this basis set has been

Table 2. Orbital energies and ionization potentials for planar 1,4-cyclohexadiene (1)

Sym	$-\epsilon$ (eV)	IP(eV) <sup>a</sup>	$\Delta$ (eV)
$\sigma_{\text{sym}}$ 3a <sub>g</sub>	30.83	-	-
2b <sub>3u</sub>	27.73	23.0	-4.7
3b <sub>2u</sub>	27.56	23.0	-4.6
4a <sub>g</sub>	23.62	20.3	-3.3
2b <sub>1g</sub>	21.19	18.6	-2.6
5a <sub>g</sub>	18.56	16.5	-2.1
4b <sub>2u</sub>	17.83	15.9	-1.9
3b <sub>3u</sub>	16.24	14.7	-1.5
4b <sub>3u</sub>	15.44	13.7	-1.7
5b <sub>2u</sub>	14.26	13.1	-1.2
6a <sub>g</sub>	13.01	12.1	-0.9
3b <sub>1g</sub>	12.14	11.0	-1.1
$\pi_{\text{sym}}$ 1b <sub>1u</sub> (SS) <sup>b</sup>	16.48	14.7	-1.8
1b <sub>3g</sub> (AS)	15.56	13.7	-1.9
1b <sub>2g</sub> (SA)	9.80	9.8	0.0
2b <sub>1u</sub> (SS)	8.85	9.0 (8.8) <sup>c</sup>	+0.2 (+0.1)

<sup>a</sup>Ref 14. <sup>b</sup>Both planes are perpendicular to the plane of the molecule, with plane 1 bisecting the double bonds and plane 2 going through C<sub>3</sub> and C<sub>6</sub> (*cf.*, ref 15). <sup>c</sup>Ref 11.

found<sup>12,13</sup> to vary smoothly with the orbital energies due to reorganization and correlation effects. A correction of -5.7 to -1.4 eV for  $\sigma$ -orbitals with the larger corrections for inner orbitals and from -1.8 to 0.0 for the  $\pi$ -orbitals has been found for benzene and azabenzenes.<sup>13</sup> As can be seen from Table 2 the corrections for the orbital energies of 1 are in good agreement with these results.

The assignment of peaks of the photoelectron spectrum made here is the same as that predicted by SPINDO calculations.<sup>14</sup> Other semiempirical calculations on 1,4-cyclohexadiene, dealing primarily with the splitting of the  $\pi$ -electron levels, also suggest SS above SA,<sup>15,16,17</sup> in accordance with the concept of through-bond coupling.<sup>15</sup>

The results of conformational studies based on *ab initio* calculations are very sensitive to the choice of basis set. Large basis sets are generally required,<sup>6</sup> but in certain cases, *e.g.*, with hydrocarbons, small basis sets are sufficient to obtain satisfactory results.<sup>18</sup> Furthermore an optimization of the geometry is often desirable. In our case this would be very time consuming and probably not necessary since the basis set used (double zeta) has been found<sup>19</sup> to give bond distances very close to experimental values. The energy difference between the planar and boat conformation of 1,4-cyclohexadiene<sup>20</sup> (1 and 2) obtained here (7.4 kcal·mol<sup>-1</sup>) is larger than that predicted by force field calculations<sup>5</sup> (1.0 kcal·mol<sup>-1</sup>). This can be due either to the lack of geometry optimization and limited basis set used in the *ab initio* calculations, or to an underestimation of electronic interactions in the force field calculations.

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