

## Molecular Structure of Bicyclo[4.2.2]decapentaene

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Extensive search over the energy surface of bicyclo[4.2.2]decapentaene with MMP2 molecular mechanics method and AM1 semiempirical MO method revealed only one, deep energy minimum structure, which corresponds to **1**. The alternative structure **2** could not be identified as a stationary point. Although the deviation of benzenoid ring from planarity is large in the energy minimum structure ( $\phi = 26^\circ$  (MMP2),  $37^\circ$  (AM1)), the bond lengths show no severe alternation.

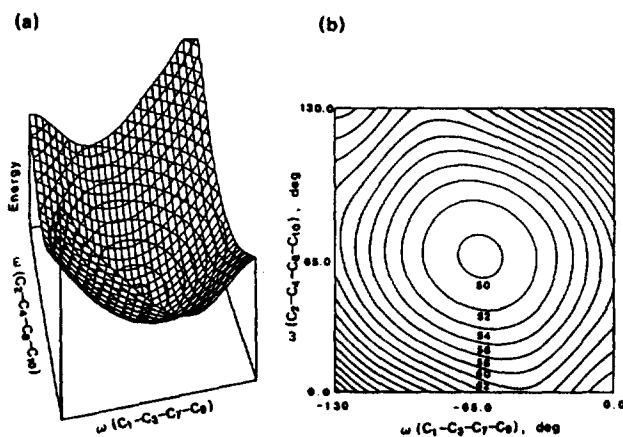
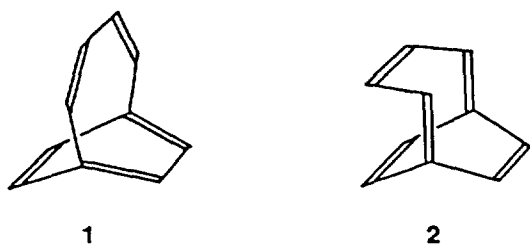
## Introduction

Geometrically distorted unsaturated compounds have attracted considerable attention because of their remarkable properties and chemical reactivities.<sup>1-7</sup> Among those compounds are cyclophanes of which structural features provide crucial informations on ring strain and aromaticity. The X-ray crystal structure analyses of [6]paracyclophanes<sup>8</sup> and [5]metacyclophane<sup>9</sup> showed that alternating bond lengths were not observed although the aromatic rings were greatly distorted from planarity. The available <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data for the most of the small [n]cyclophanes except for the very small [4]cyclophanes suggest intact aromaticity even for the smallest members of the family.<sup>10</sup> Due to their unstability [4]cyclophanes can only be detected as a transient species so that calculational results become important.

The generation of bicyclo[4.2.2]decapentaene as a transient species which can be considered to be more strained than [4]paracyclophane was recently reported by Tsuji and Nishida.<sup>11</sup> The structure of bicyclo[4.2.2]decapentaene can be envisaged as at least two unique alternatives, namely [4]paracyclophadiene (**1**) and 1,6-etheno bridged *cis,trans,cis,trans*-cyclooctatetraene (**2**). Tsuji concluded that bicyclo[4.2.2]decapentaene is best represented by the structure **1** but that a possibility of structure **2** as a local minimum on the potential surface cannot be ruled out. We present in this article the structure of bicyclo[4.2.2]decapentaene as calculated by MMP2 molecular mechanics method<sup>12</sup> and AM1 semiempirical MO method.<sup>13</sup>

## Results and Discussion

The two-parametric torsional energy surface of bicyclo[4.2.2]decapentaene was investigated in order to elucidate the relative stability of **1** and **2**. Whereas the dimensions of mole-



**Figure 1.** MMP2 torsional energy surface of bicyclo[4.2.2]decapentaene with dihedral angles at  $C_1-C_3-C_7-C_9$  and  $C_2-C_4-C_8-C_{10}$  as two variables. (a) Three-dimensional perspective. (b) Contour map. Energies in kcal/mol. See Figure 2 for numbering of atoms.

**Table 1.** MMP2-Calculated Bond Distances of Bicyclo[4.2.2]decapentaene in Å

C(1)-C(2)	1.385	C(5)-C(6)	1.385
C(1)-C(3)	1.406	C(3)-C(5)	1.407
C(2)-C(4)	1.406	C(4)-C(6)	1.407
C(3)-C(7)	1.516	C(4)-C(8)	1.516
C(7)-C(9)	1.353	C(8)-C(10)	1.353
C(9)-C(10)	1.476	C(2)-H(12)	1.104
C(1)-H(11)	1.104	C(16)-H(14)	1.104
C(5)-H(13)	1.104	C(8)-H(16)	1.103
C(7)-H(15)	1.103	C(10)-H(18)	1.104
C(9)-H(17)	1.104		

cular energy surface are generally much higher than two, there will be cases in conformational processes of small molecules where the energy surface can be more or less adequately described by taking only two dihedral angles as variables.<sup>14</sup> Two dihedral angles involving bridgehead carbon atoms were chosen to characterize the conformational energy surface.

As shown in Figure 1 only one deep energy minimum

**Table 2.** MMP2-Calculated Valence Angles of Bicyclo[4.2.2]decapentaene in Degrees

C(2)-C(1)-C(3)	118.6	C(1)-C(2)-C(4)	118.6
C(3)-C(5)-C(6)	118.6	C(4)-C(6)-C(5)	118.6
C(1)-C(3)-C(5)	115.4	C(2)-C(4)-C(6)	115.4
C(1)-C(3)-C(7)	109.0	C(2)-C(4)-C(8)	109.0
C(5)-C(3)-C(7)	109.0	C(6)-C(4)-C(8)	109.0
C(3)-C(7)-C(9)	125.8	C(4)-C(8)-C(10)	125.7
C(7)-C(9)-C(10)	133.0	C(8)-C(10)-C(9)	133.0
C(2)-C(1)-H(11)	118.0	C(1)-C(2)-C(12)	118.0
C(6)-C(5)-H(13)	118.0	C(5)-C(6)-C(14)	118.0
C(3)-C(1)-H(11)	118.7	C(4)-C(2)-C(12)	118.7
C(3)-C(5)-H(13)	118.7	C(4)-C(6)-C(14)	118.8
C(9)-C(7)-H(15)	118.7	C(10)-C(8)-C(16)	118.7
C(3)-C(7)-H(15)	115.6	C(4)-C(8)-C(16)	115.6
C(7)-C(9)-H(17)	113.7	C(8)-C(10)-C(18)	113.7
C(10)-C(9)-H(17)	113.2	C(9)-C(10)-C(18)	113.2

**Table 3.** MMP2 Energies of Bicyclo[4.2.2]decapentaene in kcal/mol<sup>a</sup>

Steric energy	Stretch	.56	(1.45)
	Bend	9.16	(8.99)
	Stretch-Bend	-.18	(-1.19)
	Non-bonded	5.94	(9.08)
	Torsion	33.50	(50.14)
	Total	48.97	(68.47)
Strain energy		57.00	(76.50)
Heat of formation		111.50	(131.63)

<sup>a</sup>The values in parenthesis pertain to **2**.

was found. According to the geometrical data (Table 1, 2) the energy minimum structure of bicyclo[4.2.2]decapentaene is [4]paracyclophadiene with  $C_{2v}$  symmetry. The bond lengths in the six-membered ring shows no remarkable alternation (1.39 Å and 1.41 Å) and the bond angles also do not deviate much from natural value (115° and 119°). Whereas, the bond lengths in the four bridge carbon atoms are much similar with 1,3-butadiene (1.48 Å and 1.35 Å) and the two bond angles of bridge carbon atoms deviate far from natural value (133°). The bond length between terminal bridge carbon and bridgehead carbon of benzenoid ring shows the single bond value (1.52 Å), and bridge carbons are completely coplanar (dihedral angle of 7, 9, 10, 8=0°). When MMP2 calculation of **2** was repeated while fixing two dihedral angles (angles of 1, 3, 7, 9 and 2, 4, 8, 10) at zero, the geometry could be optimized to give a structure with  $C_s$  point group having 20 kcal/mol higher energy than the global minimum structure (Table 3). However, when the dihedral angle constraint was removed, the structure spontaneously changed into the global minimum by geometry-optimization. Hence, it is concluded that structure **2** is not a stationary point within MMP2 energy surface.

It can be considered that when benzene ring is bent by strain the bond lengths show alternation and addition reaction is apt to be occurred. The bending of the benzene ring can be described by the two angles,  $\phi$  and  $\alpha$ , as shown in

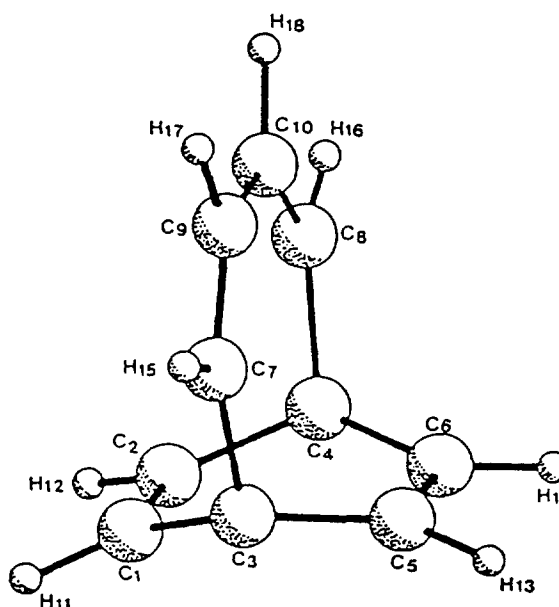
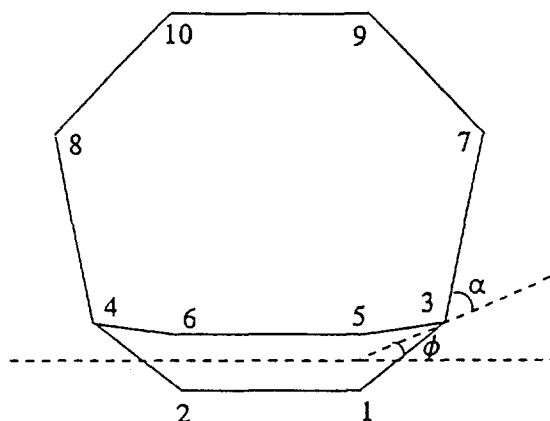
**Figure 2.** MMP2-optimized structure of bicyclo[4.2.2]decapentaene.**Figure 3.** The skeletal structure of bicyclo[4.2.2]decapentaene.

Figure 3. The  $\phi$  and  $\alpha$  values of **1** is 26° (37° by AM1) and 52° (36° by AM1), respectively. These compare well with those of [5]metacyclophane;  $\phi$  value is 26.8° by X-ray analysis and 32° by MNDO calculation.

Attempts to optimize a number of starting geometries of bicyclo[4.2.2]decapentaene with AM1 semiempirical MO method invariably gave **1** with  $C_{2v}$  symmetry (Table 4, 5). The same tendency was found by AM1 calculation result. Bond alternation in the benzenoid ring was not pronounced. Nevertheless the bond between bridge terminal carbon atom and bridgehead carbon atom shows considerable double bond character (1.46 Å) and this suggests some hyperconjugation and  $\pi$ -electron interactions between four-membered bridge and benzenoid ring, which MMP2 method failed to detect (Table 6).

Common to MMP2 and AM1 results, there occur sizable angle deformations in order to accommodate the distortion of benzenoid ring, whereas the degree of bond alternation is nearly the same as in benzene. This can be compared

**Table 4.** AM1-Calculated Bond Distances of Bicyclo[4.2.2]decapentaene in Å

C(1)-C(2)	1.391	C(5)-C(6)	1.389
C(1)-C(3)	1.421	C(3)-C(5)	1.421
C(2)-C(4)	1.421	C(4)-C(6)	1.422
C(3)-C(7)	1.464	C(4)-C(8)	1.464
C(7)-C(9)	1.357	C(8)-C(10)	1.357
C(9)-C(10)	1.463	C(2)-H(12)	1.095
C(1)-H(11)	1.095	C(6)-H(14)	1.095
C(5)-H(13)	1.095	C(8)-H(16)	1.099
C(7)-H(15)	1.098	C(10)-H(18)	1.112
C(9)-H(17)	1.112		

**Table 5.** AM1-Calculated Valence Angles of Bicyclo[4.2.2]decapentaene in Degrees

C(2)-C(1)-C(3)	114.4	C(1)-C(2)-C(4)	114.5
C(3)-C(5)-C(6)	114.4	C(4)-C(6)-C(5)	114.4
C(1)-C(3)-C(5)	117.5	C(2)-C(4)-C(6)	117.4
C(1)-C(3)-C(7)	114.7	C(2)-C(4)-C(8)	114.7
C(5)-C(3)-C(7)	114.7	C(6)-C(4)-C(8)	114.5
C(3)-C(7)-C(9)	118.3	C(4)-C(8)-C(10)	118.5
C(7)-C(9)-C(10)	135.3	C(8)-C(10)-C(9)	135.3
C(2)-C(1)-H(11)	122.3	C(1)-C(2)-H(12)	122.2
C(6)-C(5)-H(13)	122.3	C(5)-C(6)-H(14)	122.3
C(3)-C(1)-H(11)	121.8	C(4)-C(2)-H(12)	121.7
C(3)-C(5)-H(13)	121.7	C(4)-C(6)-H(14)	121.7
C(9)-C(7)-H(15)	121.3	C(10)-C(8)-H(16)	121.3
C(3)-C(7)-H(15)	120.4	C(4)-C(8)-H(16)	120.3
C(7)-C(9)-H(17)	114.5	C(8)-C(10)-H(18)	114.6
C(10)-C(9)-H(17)	110.2	C(9)-C(10)-H(18)	110.1

**Table 6.** Selected Features in Computed Structure of Bicyclo[4.2.2]decapentaene

		MMP2	AM1
Bond length/Å	C(1)-C(2)	1.385	1.391
	C(1)-C(3)	1.406	1.421
	C(3)-C(7)	1.516	1.464
	C(7)-C(9)	1.353	1.357
	C(9)-C(10)	1.476	1.463
Valence angle/Å	C(2)-C(1)-C(3)	118.6	114.4
	C(1)-C(3)-C(5)	115.4	117.5
	C(1)-C(3)-C(7)	109.0	114.7
	C(3)-C(7)-C(9)	125.8	118.3
	C(7)-C(9)-C(10)	133.0	135.3
Dihedral angle/Å	C(1)-C(3)-C(7)-C(9)	-63.4	-70.4
	C(7)-C(9)-C(10)-C(8)	0.0	0.3

with the fact that [5]metacyclophane shows chemical reactivity and UV spectrum characteristic to bent aromatic ring but has normal carbon-carbon bond lengths and ring current effect in NMR spectrum.<sup>9</sup> With these results we can conclude that there must be an effective  $\pi$ -electron delocalization in

the benzenoid ring of bicyclo[4.2.2]decapentaene, even though the compound induces cycloaddition reaction very readily.

### Computational Technique

Program MMP2(85)-PC was obtained from QCPE<sup>15</sup> and used throughout this work. A locally updated modification of MOPAC (version 3.0) was used to perform AM1 calculations.<sup>16</sup> In the drawing of three-dimensional surfaces (Figure 1),<sup>17</sup> energy values at the grid point were calculated by using spline function.<sup>18</sup>

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