

## Molecular Structure of 2,2,4,4,6,6-Hexamethyl-1,3,5-trimethylenecyclohexane As Determined by Gas-Phase Electron Diffraction

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The molecular structure of 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane has been determined in the gas phase at a nozzle tip temperature of 340 K. The electron diffraction data were found to be consistent with a model where the cyclohexane ring adopts a distorted twist-boat conformation. The averaged geometrical parameters ( $r_g$  and  $\angle_a$ ) obtained from least squares analysis are  $r(\text{C}=\text{C}) = 1.346(4)$  Å,  $r(\text{C}-\text{C})_{\text{ring}} = 1.537(1)$  Å,  $r(\text{C}-\text{C})_{\text{Me}} = 1.543(1)$  Å,  $\angle\text{C}^6\text{C}^1\text{C}^2 = 117.5(11)^\circ$ ,  $\angle\text{C}^1\text{C}^2\text{C}^3 = 113.1(12)^\circ$ , and  $\angle\text{MeCMe} = 108.2(13)^\circ$ . The experimental results are consistent with the results from HF/6-311G(d) and MP2/6-311G(d) calculations where the distorted twist-boat form is found to be lower in energy than the chair form by 9.85 and 10.7 kcal/mol, respectively.

### Introduction

It is well-known that the global minimum of cyclohexane is the chair conformation, with the twist-boat  $\sim 5.5$  kcal/mol above it.<sup>1</sup> To alter the relative stability of the chair and twist-boat conformations, structural constraints have to be introduced such as in multiple fused cyclohexane rings. For unconstrained monocyclic hydrocarbons, only a few compounds are known where the twist-boat form is preferred over the chair form. The twist-boat form is found in *cis*-1,4-*tert*-butylcyclohexane,<sup>2,3</sup> where the axial *tert*-butyl group destabilizes the chair form. The twist-boat form is also observed in 4,4,8,8,12,12-hexamethyltrispiro[2,1,2,1,2,1]dodecane,<sup>4,5</sup> where the alternating carbon atoms of the cyclohexane ring are attached to two methyl groups or a cyclopropyl group (Figure 1). When the cyclopropyl groups are opened up into two methyl groups, as in dodecamethylcyclohexane, the chair form was found to be the preferred conformation.<sup>6</sup> The presence of six methyl groups in the axial positions does not destabilize the chair form enough to make the twist-boat the global minimum. In fact, in the sterically crowded *all-trans*-1,2,3,4,5,6-hexaisopropylcyclohexane, the isopropyl groups are all located in the axial positions rather than in the equatorial positions of the chair conformation.<sup>7</sup> The twist-

boat conformer was observed in both the liquid and solid phases for 1,4-cyclohexanedione.<sup>8</sup> The stability of the twist-boat form of trispirododecane was attributed to the geometrical distortion of the cyclohexane ring forced upon by the cyclopropyl groups, since sterically this molecule is rather similar to dodecamethylcyclohexane.

This suggestion can be further probed by studying the structure and conformation of 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane, where the three cyclopropyl groups are replaced by three C=C bonds. The steric environment of the cyclohexane ring is altered in a way similar to that affected by the cyclopropyl groups in 4,4,8,8,12,12-hexamethyltrispiro[2,1,2,1,2,1]dodecane (i.e., the hybridization of three of the carbon atoms in the ring would be  $\text{sp}^2$ -like). On the other hand, the plane of the  $\text{H}_2\text{C}=\text{C}$  moiety is rotated  $90^\circ$  with respect to the CCC plane of the dimethyl and cyclopropyl moieties. We therefore initiated a gas-phase electron diffraction study on the structure and conformation of the title compound and are reporting the findings here.

### Experimental Section

A sample was prepared according to the reported procedure.<sup>5</sup> Electron diffraction diagrams were recorded<sup>9</sup> at a nozzle temperature of 340 K, using Electron Image plates, at nozzle-to-plate distances of 497.87 and 248.01 mm, and at an electron wavelength of 0.058 68 Å. Benzene was used as the calibration standard. Five plates from the long camera distances and six from the short camera distances were selected for least squares analysis. Intensity data were treated in the usual way<sup>10</sup> and were interpolated at interval units of  $q[(40/\lambda) \sin(\theta/2)]$ , and ranges for the long and short camera experiments were  $5 \leq q \leq 48$  and  $9 \leq q \leq 92$ , respectively. Least squares procedures

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(1) *Conformational Behavior of Six-membered Rings*; Juaristi, E., Ed.; VCH Publishers: New York, 1995.

(2) van Bekkum, H.; Hoefinagel, M. A.; de Lavieter, L.; van Veen, A.; Verkade, P. E.; Wemmers, A.; Wepster, B. M.; Palm, J. H.; Schafer, L.; Dekker, H.; Mosselman, C.; Somsen, G. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1363.

(3) Schebert, W. K.; Southern, J. F.; Schafer, L. *J. Mol. Struct.* **1973**, *16*, 403.

(4) Shen, Q.; Traetteberg, M. *J. Mol. Struct.* **2003**, *657*, 185.

(5) Traetteberg, M.; Bakken, P.; Fitjer, L.; Scheuermann, H. *J. Mol. Struct.* **1987**, *159*, 325.

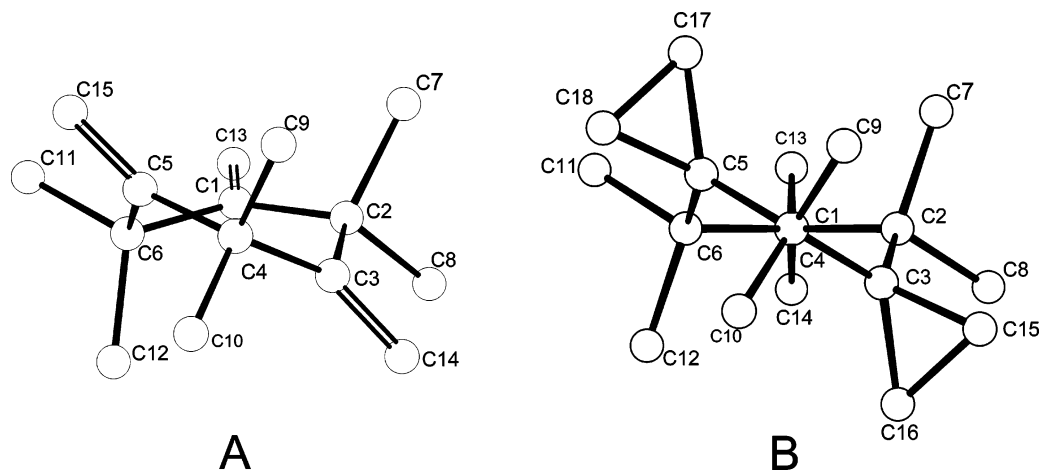
(6) Wehle, D.; Scheuermann, H. J.; Fitjer, L. *Chem. Ber.* **1986**, *119*, 3127.

(7) Golan, O.; Goren, Z.; Biali, S. E. *J. Am. Chem. Soc.* **1990**, *112*, 9300.

(8) Mossel, A.; Romers, C.; Havinga, E. *Tetrahedron Lett.* **1963**, *19*, 1247; *Acta Crystallogr.* **1964**, *17*, 1217.

(9) Zeil, W.; Haase, J.; Wegmann, L. *Z. Instrumentenk. 1966*, *74*, 84. Bastiansen, O.; Graber, R.; Wegmann, L. *Balzer's High Vacuum Rep.* **1969**, *25*, 1.

(10) Andersen, B.; Seip, H. M.; Strand, T. G.; Stolevik, R. *Acta Chem. Scand.* **1969**, *25*, 1.



**FIGURE 1.** Atomic numbering for (A) 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane and (B) 4,4,8,8,12,12-hexamethyltrispiro[2,1,2,1,2,1]dodecane, excluding hydrogen atoms.

**TABLE 1.** Results from HF and MP2 (6-311G(d)) Calculations for the Twist-Boat and Chair Forms of 2,2,4,4,6,6-Hexamethyl-1,3,5-trimethylenecyclohexane

bond	twist-boat		chair		angle	twist-boat		chair		
	HF	MP2	HF	MP2		HF	MP2	HF	MP2	
	Six-Ring					Six-Ring				
C <sup>3</sup> –C <sup>4</sup>	1.5442	1.5322	1.5481	1.5373	∠C <sup>2</sup> C <sup>3</sup> C <sup>4</sup>	118.2	117.4	119.4	119.5	
C <sup>4</sup> –C <sup>5</sup>	1.5399	1.5286	1.5480	1.5384	∠C <sup>3</sup> C <sup>4</sup> C <sup>5</sup>	110.1	109.1	109.3	108.9	
C <sup>5</sup> –C <sup>6</sup>	1.5374	1.5282	1.5481	1.5373	∠C <sup>4</sup> C <sup>5</sup> C <sup>6</sup>	116.9	116.7	119.4	119.5	
C <sup>6</sup> –C <sup>1</sup>	1.5337	1.5265	1.5481	1.5384	∠C <sup>5</sup> C <sup>6</sup> C <sup>1</sup>	106.5	106.6	109.3	108.9	
C <sup>1</sup> –C <sup>2</sup>	1.5484	1.5376	1.5480	1.5373	∠C <sup>6</sup> C <sup>1</sup> C <sup>2</sup>	117.8	117.4	119.4	119.5	
C <sup>2</sup> –C <sup>3</sup>	1.5423	1.5291	1.5481	1.5384	∠C <sup>1</sup> C <sup>2</sup> C <sup>3</sup>	111.7	110.9	109.3	108.9	
	C=C Bonds					Me–C–Me				
C <sup>3</sup> –C <sup>14</sup>	1.3228	1.3479	1.3248	1.3503	∠C <sup>9</sup> C <sup>4</sup> C <sup>10</sup>	105.7	105.3	103.3	103.5	
C <sup>5</sup> –C <sup>15</sup>	1.3224	1.3475	1.3248	1.3503	∠C <sup>7</sup> C <sup>2</sup> C <sup>8</sup>	107.3	107.7	103.3	103.5	
C <sup>1</sup> –C <sup>13</sup>	1.3222	1.3469	1.3248	1.3503	∠C <sup>11</sup> C <sup>6</sup> C <sup>12</sup>	105.8	106.7	103.3	103.5	
	Methyl Groups					C–C–Me				
C <sup>4</sup> –C <sup>9</sup>	1.5484	1.5452	1.5420	1.5377	∠C <sup>9</sup> C <sup>4</sup> C <sup>3</sup>	108.9	109.2	110.7	110.7	
C <sup>4</sup> –C <sup>10</sup>	1.5493	1.5465	1.5530	1.5502	∠C <sup>10</sup> C <sup>4</sup> C <sup>3</sup>	111.9	112.3	111.3	111.3	
C <sup>2</sup> –C <sup>8</sup>	1.5402	1.5332	1.5520	1.5502	∠C <sup>9</sup> C <sup>4</sup> C <sup>5</sup>	112.1	112.6	110.4	110.4	
C <sup>2</sup> –C <sup>7</sup>	1.5501	1.5478	1.5430	1.5377	∠C <sup>10</sup> C <sup>4</sup> C <sup>5</sup>	108.1	108.5	111.9	111.9	
C <sup>6</sup> –C <sup>11</sup>	1.5346	1.5297	1.5420	1.5377	∠C <sup>7</sup> C <sup>2</sup> C <sup>3</sup>	111.0	111.2	110.4	110.4	
C <sup>6</sup> –C <sup>12</sup>	1.5501	1.5466	1.5530	1.5502	∠C <sup>8</sup> C <sup>2</sup> C <sup>3</sup>	108.9	109.2	111.9	111.9	
	Dihedral Angles, Six-Ring					∠C <sup>1</sup> C <sup>2</sup> C <sup>7</sup>	109.7	110.8	110.7	110.7
∠C <sup>2</sup> C <sup>3</sup> C <sup>4</sup> C <sup>5</sup>	29.9	30.0	–45.65	–46.23	∠C <sup>1</sup> C <sup>2</sup> C <sup>8</sup>	108.2	106.9	111.3	111.3	
∠C <sup>3</sup> C <sup>4</sup> C <sup>5</sup> C <sup>6</sup>	25.6	28.9	45.61	46.26	∠C <sup>5</sup> C <sup>6</sup> C <sup>12</sup>	111.6	111.7	111.3	111.3	
∠C <sup>4</sup> C <sup>5</sup> C <sup>6</sup> C <sup>1</sup>	–61.9	–63.3	–45.62	–46.25	∠C <sup>5</sup> C <sup>6</sup> C <sup>11</sup>	111.9	111.8	110.7	110.7	
∠C <sup>5</sup> C <sup>6</sup> C <sup>1</sup> C <sup>2</sup>	43.7	38.7	45.65	46.25	∠C <sup>1</sup> C <sup>6</sup> C <sup>12</sup>	112.1	112.3	111.9	111.9	
∠C <sup>6</sup> C <sup>1</sup> C <sup>2</sup> C <sup>3</sup>	5.6	13.4	–45.69	–46.23	∠C <sup>1</sup> C <sup>6</sup> C <sup>11</sup>	109.0	107.8	110.4	110.4	
∠C <sup>1</sup> C <sup>2</sup> C <sup>3</sup> C <sup>4</sup>	–45.8	–51.6	45.69	46.26						

outlined by Gundersen and Hedberg<sup>11</sup> were followed using elastic scattering factors tabulated by Schaffer, Yates, and Bonham.<sup>12</sup>

**Theoretical Calculations.** Ab initio molecular orbital calculations<sup>13</sup> were carried out at both the HF and MP2 levels of theory using the 6-311G(d) basis set. The optimized geometries for both the chair and twist-boat forms were obtained, and the former was found to be higher in energy (10.7 (MP2) and 9.85 (HF) kcal/mol). Frequency calculations were also carried out, and both were minima on the potential energy surface. The geometrical parameters for these two conformers obtained from these calculations are summarized in Table 1.

**Electron Diffraction.** Amplitudes of vibration were calculated using a force field converted from the one used for 4,4,8,8,12,12-hexamethyltrispiro[2,1,2,1,2,1]dodecane.<sup>6</sup> The force constants related to the cyclopropyl group are replaced by the following values: stretch, C=C (9.5 mdyn/Å), H–C(=) (5.5

mdyn/Å); bend, C=CC (1.0 mdyn Å/rad<sup>2</sup>), HC=C (0.80 mdyn Å/rad<sup>2</sup>), CC(=)C (1.0 mdyn Å/rad<sup>2</sup>), HC(=)H (0.32 mdyn Å/rad<sup>2</sup>); out-of-plane bends (0.20 mdyn Å/rad<sup>2</sup>); and C=C torsion (0.27 mdyn Å/rad<sup>2</sup>).<sup>14</sup>

Theoretical calculations showed that the low energy form does not have a perfect twist-boat form. It resembles a slightly distorted boat, with the bottom of the boat twisted slightly from

(11) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(12) Schaffer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

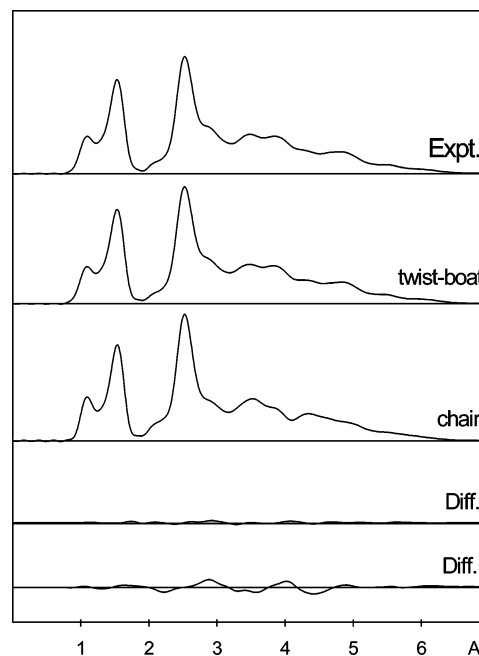
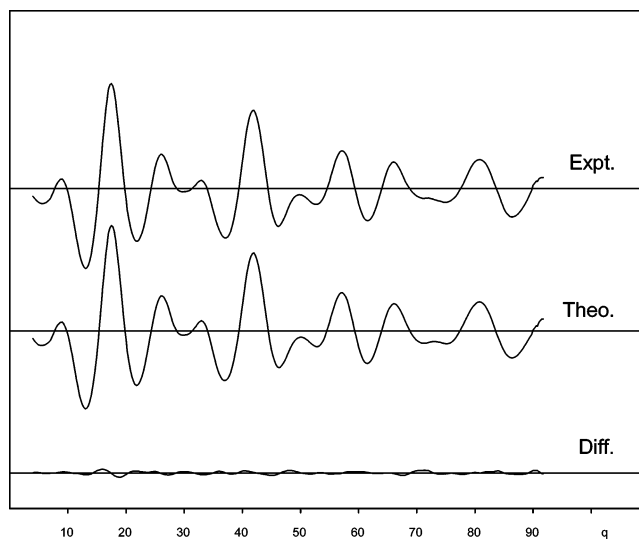
**TABLE 2. Structural Results From Least Squares Analyses of Electron Diffraction Data for 2,2,4,4,6,6-Hexamethyl-1,3,5-trimethylenecyclohexane<sup>a</sup>**

parameter	value	parameter	value
$r(\text{C-H})_{\text{av}}$	1.106(4)	$\angle\text{C}^2\text{C}^1\text{C}^6$	117.5(11)
$r(\text{C=C})$	1.346(4)	$\angle\text{C}^7\text{C}^2\text{C}^1$	110.9(6)
$r(\text{C-C})_{\text{av}}$	1.540(2)	$\angle\text{HC}^7\text{C}^2$	114.5(20)
$D_1$	0.006 (fixed)	$\tau\text{HC}^7\text{C}^2\text{C}^1$	60.0 (fixed)
$D_2$	0.007 (fixed)	flap 1	161.6(25)
		flap 2	130.3(24)
Dependent Values <sup>b</sup>			
Cyclohexane <sup>b</sup>			
$\text{C}^1\text{-C}^2$	1.548	$\angle\text{C}^6\text{C}^1\text{C}^2$	117.5(11)
$\text{C}^2\text{-C}^3$	1.540	$\angle\text{C}^1\text{C}^2\text{C}^3$	113.1(12)
$\text{C}^3\text{-C}^4$	1.540	$\angle\text{C}^2\text{C}^3\text{C}^4$	117.3(11)
$\text{C}^4\text{-C}^5$	1.532	$\angle\text{C}^3\text{C}^4\text{C}^5$	110.7(14)
$\text{C}^5\text{-C}^6$	1.532	$\angle\text{C}^4\text{C}^5\text{C}^6$	116.8(11)
$\text{C}^6\text{-C}^1$	1.532	$\angle\text{C}^5\text{C}^6\text{C}^1$	105.5(14)
Methyl Group <sup>b</sup>		Me-C-Me	
$\text{C}^2\text{-C}^7$	1.548	$\angle\text{C}^7\text{C}^2\text{C}^8$	107.6(31)
$\text{C}^2\text{-C}^8$	1.540	$\angle\text{C}^9\text{C}^4\text{C}^{10}$	108.4(34)
$\text{C}^4\text{-C}^9$	1.548	$\angle\text{C}^{11}\text{C}^6\text{C}^{12}$	108.8(34)
$\text{C}^4\text{-C}^{10}$	1.540		
$\text{C}^6\text{-C}^{11}$	1.532		
$\text{C}^6\text{-C}^{12}$	1.548	$\angle\text{C}^7\text{C}^2\text{C}^1/\angle\text{C}^8\text{C}^2\text{C}^1$ <sup>c</sup>	110.9/107.9(6)
Dihedral Angles		$\angle\text{C}^9\text{C}^4\text{C}^5/\angle\text{C}^9\text{C}^4\text{C}^3$ <sup>d</sup>	110.9/107.9(6)
$-\text{C}^1\text{C}^2\text{C}^3\text{C}^4$	43.4(31)	$\angle\text{C}^{11}\text{C}^6\text{C}^5/\angle\text{C}^{11}\text{C}^6\text{C}^1$ <sup>e</sup>	110.9/107.9(6)
$-\text{C}^2\text{C}^3\text{C}^4\text{C}^5$	27.4(12)		
$-\text{C}^3\text{C}^4\text{C}^5\text{C}^6$	27.3(12)		
$-\text{C}^4\text{C}^5\text{C}^6\text{C}^1$	-62.7(24)		
$-\text{C}^5\text{C}^6\text{C}^1\text{C}^2$	-44.3(24)		
$-\text{C}^6\text{C}^1\text{C}^2\text{C}^3$	4.2(31)		

<sup>a</sup> Distances in angstroms and angles in degrees; the C-C single bonds belong to three groups [ $r(\text{C-C})_{\text{av}}$ ,  $r(\text{C-C})_{\text{av}} + D_1$ , and  $r(\text{C-C})_{\text{av}} - D_2$ ]; flap 1 is the angle between planes formed by atoms 6, 1, and 2 and 1, 4, and 2, and flap 2 is the angle between planes formed by atoms 2, 3, and 4 and 6, 2, and 4 which is equal to that between atoms 4, 5, and 6 and 6, 2, and 4. <sup>b</sup> Uncertainties in bond distances and valence angles are 0.002 Å and 2°, respectively. <sup>c</sup>  $\angle\text{C}^7\text{C}^2\text{C}^1 = \angle\text{C}^7\text{C}^2\text{C}^3/\angle\text{C}^8\text{C}^2\text{C}^1 = \angle\text{C}^8\text{C}^2\text{C}^3$ . <sup>d</sup>  $\angle\text{C}^9\text{C}^4\text{C}^5 = \angle\text{C}^{10}\text{C}^4\text{C}^3/\angle\text{C}^9\text{C}^4\text{C}^3 = \angle\text{C}^{10}\text{C}^4\text{C}^5$ . <sup>e</sup>  $\angle\text{C}^{11}\text{C}^6\text{C}^5 = \angle\text{C}^{12}\text{C}^6\text{C}^1 = \angle\text{C}^{12}\text{C}^6\text{C}^5/\angle\text{C}^{11}\text{C}^6\text{C}^1$ .

the four-atom plane. As a result, the symmetry of this form is very low ( $C_1$ ). Instead of introducing twelve different C-C single bond lengths, they were grouped into three using an averaged value and two differences,  $D_1$  and  $D_2$ , which were later fixed at the calculated values. All the C-H bond lengths are assumed to be identical. The valence angle  $\angle\text{C}^6\text{C}^1\text{C}^2$  is assumed to be larger than  $\angle\text{C}^2\text{C}^3\text{C}^4$  and  $\angle\text{C}^4\text{C}^5\text{C}^6$  by the calculated amount. The structural parameters chosen to define the twist-boat form are as follows:  $r(\text{C-H})_{\text{av}}$ ,  $r(\text{C=C})$ ,  $r(\text{C-C})_{\text{av}}$ ,  $D_1$ ,  $D_2$ ,  $\angle\text{C}^6\text{C}^1\text{C}^2$ ,  $\angle\text{C}^7\text{C}^2\text{C}^1 = \angle\text{C}^7\text{C}^2\text{C}^3$ ,  $\angle\text{HC}^7\text{C}^2$ , flap 1 (angle between planes formed by carbon atoms  $\text{C}^6$ ,  $\text{C}^1$ , and  $\text{C}^2$  and  $\text{C}^1$ ,  $\text{C}^4$ , and  $\text{C}^2$ ), flap 2 (angle between planes formed by atoms  $\text{C}^2$ ,  $\text{C}^3$ , and  $\text{C}^4$  and  $\text{C}^6$ ,  $\text{C}^2$ , and  $\text{C}^4$  which is equal to that between atoms  $\text{C}^4$ ,  $\text{C}^5$ , and  $\text{C}^6$  and  $\text{C}^6$ ,  $\text{C}^2$ , and  $\text{C}^4$ ), and  $\tau\text{HC}^7\text{C}^2\text{C}^1 = 60^\circ$ .  $\angle\text{C}^8\text{C}^2\text{C}^1$  was tied to  $\angle\text{C}^7\text{C}^2\text{C}^1$  by the calculated difference from the MP2 calculation.

The least squares refinements were performed on the molecular intensity data, on the basis of a  $r_\alpha$  molecular model. Initially the three C-C groups were assigned as follows: the cyclohexane will have two different C-C bonds with a difference, and all the methyl C-C bonds are identical with another value which is at a fixed value from one of the C-C bond groups of the ring. However, closer inspection of the HF and MP2 results (Table 1) showed that a better grouping of the C-C single bonds would be to have three groups [ $r(\text{C-C})_{\text{av}}$ ,  $r(\text{C-C})_{\text{av}} + D_1$ , and  $r(\text{C-C})_{\text{av}} - D_2$ ] and assign the twelve C-C bonds to one of these three groups and refine  $r(\text{C-C})_{\text{av}}$ . The

**FIGURE 2.** Experimental radial distribution curve and radial distribution curves for the twist-boat and chair models and their corresponding difference curves.**FIGURE 3.** Experimental and theoretical (twist-boat form) intensity curves for 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane and the corresponding difference curve.

values for  $D_1$  and  $D_2$  are obtained from the differences between the averages of these three values from HF and MP2 calculations. HF and MP2 calculations gave slightly different  $D_1$  and  $D_2$  values and a difference distribution of the C-C bonds among these three groups. As a result, two models, one with the C-C bond distribution consistent with HF and the other with MP2 calculations, were tested. The agreement between the experimental data and these two models was virtually identical. However, the torsional angles of the cyclohexane obtained from both models were closer to the HF results, and in our final refinement, the HF constraints were imposed on the theoretical model. An  $R$  factor of 5.7% was obtained for the twist-boat form. The geometrical parameters are summarized in Table 2, and the corresponding radial distribution and intensity curves are shown in Figures 2 and 3, respectively.

(14) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*, McGraw-Hill: New York, 1955.

**TABLE 3. Structural Results for 2,2,4,4,6,6-Hexamethyl-1,3,5-trimethylenecyclohexane (HMTMC6) and 4,4,8,8,12,12-Hexamethyltrispiro[2,1,2,1,2,1]dodecane (HMTSC12)<sup>a</sup>**

parameter	HMTMC6 <sup>c</sup>	HMTSC12 <sup>d</sup>
$r(\text{C}-\text{C})_{\text{ring}}^b$	1.537(1)	1.567(3)
$r(\text{C}-\text{C})_{\text{Me}}^b$	1.543(1)	1.549(5)
$\angle(\text{CCC})_{\text{ring}}^b$	117.3(11)	117(2)
	109.9(14)	109.0(22)
$\angle(\text{Me}-\text{C}-\text{Me})^b$	108.2(13)	104.7(20)
$\tau\text{C}^6\text{C}^1\text{C}^2\text{C}^3$	4.2(31)	27.9(10)
$\tau\text{C}^1\text{C}^2\text{C}^3\text{C}^4$	-44.3(24)	-61.3(22)
$\tau\text{C}^2\text{C}^3\text{C}^4\text{C}^5$	27.4(12)	31.3(14)
$\tau\text{C}^3\text{C}^4\text{C}^5\text{C}^6$	27.3(12)	31.3(14)
$\tau\text{C}^4\text{C}^5\text{C}^6\text{C}^1$	-62.7(24)	-61.3(22)
$\tau\text{C}^5\text{C}^6\text{C}^1\text{C}^2$	43.4(31)	27.9(10)

<sup>a</sup> Distances in angstroms and angles in degrees. <sup>b</sup> The bond distances and the valence angles presented are averaged values. <sup>c</sup> This work. <sup>d</sup> Reference 5.

A model representing the chair conformation was also tested. HF calculations suggested a single ring C—C bond, a single methyl C—C bond, and a ring dihedral angle of 45.6°, while MP2 showed two ring C—C bonds with a difference of 0.005 Å and a ring dihedral angle of 46.3°. We decided to use the HF constraint on the chair form to test the experimental data. The best chair form gave an *R* factor of 13%, and the radial distribution is shown in Figure 2. The principal geometrical parameter values obtained from the least squares analysis for the chair form are as follows:  $r(\text{C}=\text{C}) = 1.334(11)$  Å,  $r(\text{C}-\text{C})_{\text{ring}} = 1.538(3)$  Å,  $r(\text{C}-\text{Me}) = 1.548(3)$  Å,  $\angle\text{C}^6\text{C}^1\text{C}^2 = 115.9(16)^\circ$ ,  $\angle\text{C}^1\text{C}^2\text{C}^3 = 110.9(17)^\circ$ , and  $\tau\text{C}^1\text{C}^2\text{C}^3\text{C}^4 = 48.6(24)^\circ$ .

## Discussion

A distorted twist-boat form was observed in both the gas-phase experiment and the theoretical calculations for 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane (HMTMC6). The bond distances, valence angles, and dihedral angles are in agreement between the experiment and the calculations. The dihedral angles clearly showed that the molecule adopted a distorted twist-boat form. The C—C single bond lengths are in the range 1.532–1.548 Å. The observed C=C bond length has a value of 1.346(4) Å.

Table 3 summarizes the averaged values for the major structural parameters of the twist-boat forms of 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane (HMTMC6) and 2,2,4,4,6,6-hexamethyltrispiro[2,1,2,1,2,1]dodecane (HMTSC12). The C—C<sub>Me</sub> bond lengths in both molecules are ~1.545 Å. The average C—C bond length of the six-membered ring in HMTMC6 (1.537(1) Å) is 0.030 Å shorter than the ones observed in HMTSC12 (1.567(3) Å). The C—C<sub>Cp</sub> (Cp = cyclopropyl) bond length in methylcyclopropane<sup>15</sup> is 1.517(2) Å, and the =C—CH<sub>3</sub> bond length in isobutene<sup>16</sup> is 1.508(2) Å. The C<sub>sp<sup>3</sup></sub>—C<sub>sp<sup>2</sup></sub>/C<sub>sp<sup>3</sup></sub>—C<sub>Cp</sub> bonds in HMTMC6 and HMTSC12 are therefore longer than those in isobutene and methylcyclopropane, and the lengthening is larger in HMTSC12 (0.050 Å) than in HMTMC6 (0.029 Å).

The average valence CCC angles are 117(1)° and 110(1)° in HMTMC6 and 117(2)° and 109(2)° in HMTSC12. There is accordingly no significant difference in the

**TABLE 4. Results from MM2 Energy Calculations for Cyclohexane, Trimethylenecyclohexane (TMC6), and Trispirocyclohexane (TSC12) and the Monomethylated Compounds (in kcal/mol)<sup>a</sup>**

		cyclohexane	TMC6	TSC12
parent	chair	6.56	4.54	39.89
	twist-boat	11.93	6.96	47.93
2-methyl	chair (a)	8.67	6.99	41.81
	chair (e)	6.81	7.69	45.64
	twist-boat (a)	14.07	8.75	50.11
4-methyl	twist-boat (e)	12.31	9.89	52.48
	twist-boat	12.78	8.89	51.18

<sup>a</sup> axial = (a), equatorial = (e).

CCC valence angles of the six-membered ring between the presence of the cyclopropyl or methylene groups. However, the dihedral angles clearly show that HMTSC12 exists in a twist-boat form, while HMTMC6 adopts a distorted twist-boat form. These dihedral angles are reproduced in both HF and MP2 calculations.

Preliminary molecular mechanics calculations on cyclohexane, 1,3,5-trispirododecane (TSC12), 1,3,5-trimethylenecyclohexane (TMC6), and their monomethyl-substituted compounds were carried out to explore the chair/twist-boat energy gap (see Table 4). The calculations show that the difference between the twist-boat and the chair forms is smaller in TMC6 (2.4 kcal/mol) than in cyclohexane (5.4 kcal/mol) and in TSC12 (8.0 kcal/mol). The chair/twist-boat energy gaps for the monomethyl-substituted compounds were calculated to be 1.76 (TMC6), 5.4 (cyclohexane), and 8.3 kcal/mol (TSC12) when the methyl group is at the axial position. When the methyl group is at the equatorial position, the corresponding gaps are 2.2, 6.8, and 5.5 kcal/mol. Within the chair forms of TMC6 and TSC12, the axial methyl group is favored over the equatorial one by 0.7 and 3.8 kcal/mol, respectively, while for cyclohexane the equatorial form is favored by 1.9 kcal/mol.

The calculated energies for the parents and monomethylated compounds suggest the following:

(a) Compared to the case of the conformers of cyclohexane, the presence of the methylene groups in TMC6 destabilizes the chair form relative to the twist-boat form, while the cyclopropyl groups in TSC12 make the chair form relatively more stable.

(b) The presence of a methyl group in the axial position decreases the chair/twist-boat energy gap for TMC6, while the energy gap for TSC12 increases. The cyclohexane energy gap is hardly affected. With the methyl group at the equatorial position, the chair/twist-boat gaps for both TMC6 and TSC6 are lowered with no change for cyclohexane.

(c) A methyl group introduced in the TSC12 chair form has a drastic effect on the stability of the axial position relative to the equatorial one (3.8 kcal/mol in favor of the axial form). The difference between the methyl-substituted twist-boat forms is 2.4 kcal/mol in favor of the axial form.

(d) TMC6 has a very small energy gap between chair and twist-boat forms and would require less methyl groups to reverse the energy gap, since one methyl group changes the gap from 2.4 to 1.76 kcal/mol.

(15) Klein, A. W.; Schrupf, G. *Acta Chem. Scand.* **1981**, A35, 425.  
 (16) Tokue, J.; Fukuyama, T.; Kuchitsu, K. *J. Mol. Struct.* **1974**, 23, 33.



Molecular mechanics calculations showed that the presence of three methyl groups was necessary to reverse the gap in TMC6, while five methyl groups were needed for TSC12. For HMTMC6, the calculations showed that the distorted twist-boat form was 58 kcal/mol lower in energy than the near planar chair form. The calculated torsional angles were within 12° of the experimental values. To further understand the conformational stability of these systems, detailed analysis of results from more molecular mechanics calculations and theoretical

calculations at the HF and/or MP2 level are needed, and we are in the process of pursuing them.

**Supporting Information Available:** Starting and optimized atomic coordinates and energies for the twist-boat (HF/6-311G(d), MP2/6-311G(d)) and chair (HF/6-311G(d) and MP2/6-311G(d)) forms and the frequencies for the twist-boat form (HF/6-311G(d)) of 2,2,4,4,6,6-hexamethyl-1,3,5-trimethylenecyclohexane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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