

## Refinement of Molecular Mechanics Parameters for Deformed Benzene Based on *ab initio* Molecular Orbital Calculations

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The geometries and energies of deformed benzenes have been calculated by molecular mechanics with implementation of newly refined in-plane angle-bending-force constants and torsion parameters including those of the  $C_{ar}-C_{ar}$  bond, based on the deformation energies of benzene, toluene, and *o*-xylene obtained by MP4(SDQ)/6-31G\* level *ab initio* molecular orbital calculations. The calculated geometries of cyclophanes and tetra-*t*-butylbenzene and the internal rotational barrier height of 2-isopropyl-1,3,5-trimethyl benzene agree well with the experimental values.

The benzene ring has long been considered to behave like a rigid hexagonal plate with some definite thickness. However, in 1973, Wynberg suggested that the phenyl ring can be deformed with considerable ease.<sup>1</sup> More and more examples of deformed benzene rings became known, not only in cyclophanes under massive strain induced by short alkylene chains,<sup>2</sup> but also in congested benzenes as described later in this paper.

One can readily anticipate that the dynamic behaviour of the phenyl ring can be advantageously described by molecular mechanics.<sup>3</sup> In the MM2 method,<sup>3</sup> phenyl rings are treated 'mechanically' by using a special atom type for the aromatic carbon atoms,<sup>4</sup> having parameters slightly different from those of an  $sp^2$ -carbon atom. This strategy works well as long as the phenyl group is not under strain and retains its nearly planar hexagonal shape.<sup>5</sup>

Naturally, Allinger's 'MMP' method, where molecular mechanics and  $\pi$ -SCF MO calculations are combined,<sup>6</sup> should, in principle, be more suitable than the mechanical approach to this problem. However, in MMP2[MMP2(82)] calculations,<sup>6c</sup> the phenyl ring was deformed more readily and the calculated barrier heights for internal rotation of a bulky substituent on the benzene ring were lower than calculated by other methods. It is only recently that the previously too small torsional parameters related to the out-of-plane deformations were found to be responsible for this discrepancy, and a corrected version of MMP2 [MMP2(85)] has since appeared.<sup>7</sup>

In this paper we describe an application of the 'mechanical' approach<sup>4,5c-e</sup> to the calculations of molecules with a deformed benzene ring using newly refined parameters based on the energies obtained by *ab initio* molecular orbital calculations. The idea of calibrating the molecular mechanics force field against computed, rather than experimental, data is not new,<sup>8</sup> but available computer power has only just reached the level sufficient to carry out *ab initio* calculations of such large molecules as benzene at high levels of sophistication.

**Computational Technique.**—*ab initio* Calculations were performed on a Cray X-MP computer using the GAUSSIAN 82 program package,<sup>9</sup> with the 6-31G\* basis set.<sup>10</sup> The default-convergence criteria for SCF and geometry optimization were used. Electron correlation energy was corrected by 4th-order Møller-Plesset perturbation.<sup>11</sup> MM2<sup>3</sup> and BIGSTRN-3<sup>12</sup> programs were used for molecular mechanics calculations. The geometries of saddle-point conformers were optimized by the procedure shown in previous papers.<sup>5a,5e</sup>

### Results and Discussion

**Molecular Mechanics Parameters.**—Molecular mechanics

parameters were taken from MM2<sup>3,4</sup> force fields. Parameters for nonbonded interactions were taken from the MM2' force field<sup>13</sup> to avoid the deficiencies of the description of this interaction by the MM2 force field.<sup>13</sup> The bending-force constants and torsional parameters, including  $C_{ar}-C_{ar}$  bonds, have been newly refined, because the values of these parameters would greatly affect the amplitude of the calculated deformation of the molecules which we are going to calculate.

Our strategy in the refinement of parameters was as follows. First the total energy ( $E_{eq}$ ) of the equilibrium geometry of benzene was calculated by an *ab initio* method. Next the optimized geometry of planar, hexagonal benzene was partially and variously deformed as shown in Figure 1. The total energies were recalculated for the deformed geometries. Deformation energy ( $DE$ ) is defined as the increase in the total energy of a deformed benzene ( $E_{def}$ ) calculated by the same method as  $E_{eq}$  [equation (1)].  $DE$ s of toluene and *o*-xylene were also cal-

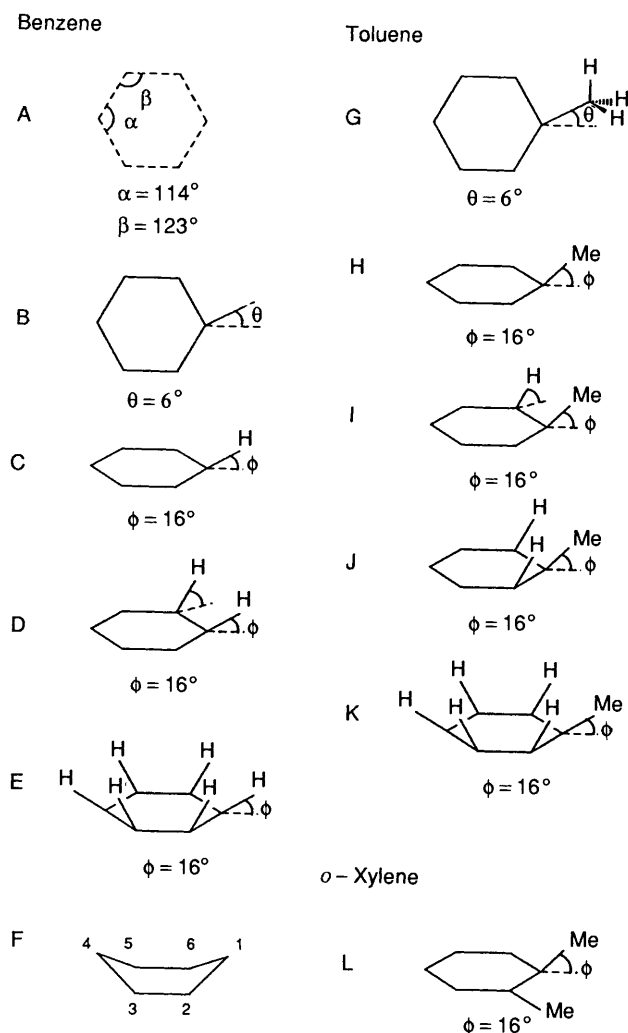
$$DE = E_{def} - E_{eq} \quad (1)$$

culated in order to include alkylbenzenes in the calculations. The calculated  $DE$ s are summarized in the second column of Table 1.

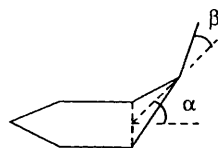
$DE$ s were also calculated by MMP2(82) and MMP2(85) methods. They are compared with the *ab initio*  $DE$ s in Table 1. One immediately notices that MMP2(82)  $DE$ s are uniformly smaller than *ab initio*  $DE$ s. This comparison confirms our previous impression that the benzene ring deforms more easily than it should when calculations are performed with MMP2(82). Especially noteworthy are the negative  $DE$ s for modes E and K, which means that MMP2(82) prefers these deformed forms to the equilibrium  $D_{6h}$  structure! MMP2(85)  $DE$ s are closer to the *ab initio*  $DE$ s than are MMP2(82)  $DE$ s.

The in-plane bending-force constants and torsional parameters were refined to reproduce the *ab initio*  $DE$ s. The newly refined in-plane bending-force constants for 1-30-30, 5-30-30, and 30-30-30 angles are 0.708, 0.542, and 1.016 mdy  $\text{\AA}$ , respectively.† These values are significantly larger than the corresponding values of 0.55, 0.36, and 0.43 used in MM2 and MMP2 calculations.  $V_1$  and  $V_3$  torsional parameters are assumed to be 0.0, and  $V_2$  parameters were refined. The refined  $V_2$  torsional parameters for 1-30-30-1, 1-30-30-5, 1-30-30-30, 5-30-30-5, 5-30-30-30, and 30-30-30-30 are 3.33, 3.85, 11.62, 4.53, 8.35,

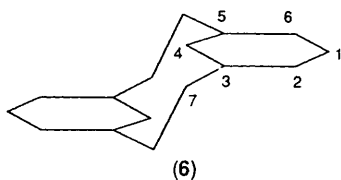
† 1 dyn =  $10^{-5}$  N. Definition of atom type: type 1 is for  $sp^3$ -carbon, 5 is for hydrogen, and 30 is for aromatic carbon.



**Figure 1.** Deformation modes of benzene, toluene, and *o*-xylene. Throughout these structures, except for the deformations specified, bond lengths, valence angles, and dihedral angles are fixed to those of the equilibrium values. In structures A and F, each hydrogen atom is on the bisector of the C-C-C angle. In structure F, the C<sup>2</sup>-C<sup>1</sup>-C<sup>6</sup> angle is 120.0°, the C<sup>1</sup>-C<sup>2</sup>-C<sup>3</sup> angle is 117.9°, the C<sup>1</sup>-C<sup>2</sup>-C<sup>3</sup>-C<sup>4</sup> dihedral angle is 0.0°, and the C<sup>2</sup>-C<sup>3</sup>-C<sup>4</sup>-C<sup>5</sup> dihedral angle is 23.51°.



**Figure 2.** Definition of ring-deformation angles of cyclophanes.



**Figure 3.** Numbering of [2.2]-*meta*-cyclophane (6).

and 5.61 kcal mol<sup>-1</sup>,\* respectively. After these adjustments had been made, *ab initio* DEs were sufficiently well reproduced (Table 1, column 3).

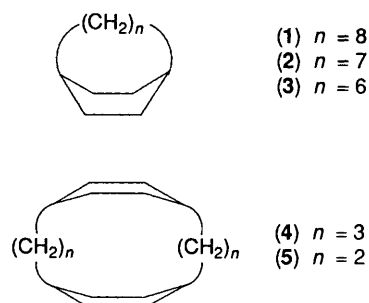
*Performance of Newly Refined Parameters for Deformed*

**Table 1.** Deformation energies of benzene, toluene, and *o*-xylene.<sup>a</sup>

Deformation mode <sup>b</sup>	Deformation energies (DE)/kcal mol <sup>-1</sup>			
	<i>ab initio</i> <sup>c</sup>	This work <sup>d</sup>	MMP2 (1982)	MMP2 (1985)
<b>Benzene</b>				
A	3.235	3.238	1.665	1.665
B	0.899	0.900	0.640	0.641
C	2.612	2.621	0.904	2.504
D	4.513	4.414	0.685	3.285
E	10.766	10.754	-1.304	4.681
F	17.643	17.642	9.504	13.249
<b>Toluene</b>				
G	1.400	1.401	1.289	1.288
H	3.207	3.235	1.416	3.960
I	5.072	5.136	1.270	5.300
J	7.006	7.038	1.136	6.344
K	11.704	11.595	-0.645	6.109
<b><i>o</i>-Xylene</b>				
L	3.216	3.215	1.452	4.034

<sup>a</sup> Definition of deformation energy is shown in text. <sup>b</sup> See Figure 1. <sup>c</sup> Calculated at MP4(SDQ)/6-31G\* level. Calculated total energies of benzene, toluene, and *o*-xylene for the equilibrium geometries are -231.492 07, -270.672 58, and -309.853 21 hartree, respectively. <sup>d</sup> Calculated by our force field.

**Benzene Rings.—Cyclophanes (1)–(10).** The ring deformation angles ( $\alpha$  and  $\beta$ ; definition shown in Figure 2<sup>14</sup>) for the geometries of five *para*-cyclophanes optimized by our force field are compared with the experimental (X-ray) values<sup>15</sup> (Table 2). The calculated deformation angles agree satisfactorily with the experimental values.



The molecular structure of compound (4) obtained by X-ray crystallography<sup>15d</sup> is close to a C<sub>2h</sub> structure. Our calculations give two energy-minimum conformers (C<sub>2h</sub> and C<sub>2v</sub>). The calculated energy difference is 0.1 kcal mol<sup>-1</sup>, which agrees with the experimental observation that boat and chair conformers exist in CDCl<sub>3</sub>-CDCl<sub>2</sub>F solution.<sup>16</sup> The barrier height for the interconversion of these conformers is calculated to be 11.3 kcal mol<sup>-1</sup>, which is close to the experimental value of  $\Delta G^\ddagger$  11.7 ± 0.5 kcal mol<sup>-1</sup> in the same solution.<sup>16</sup>  $\Delta H^\ddagger$  values of *trans*-1-methyl-3-X-substituted [3.3]-*para*-cyclophanes (X = methyl, styryl,  $\alpha$ -methylstyryl, or indenyl) have been measured to be 7.0 ± 0.3, 6.9 ± 0.8, 7.1 ± 0.4, and 4.7 ± 0.6 kcal mol<sup>-1</sup> respectively.<sup>17</sup> The introduction of small charges on the carbon and hydrogen atoms of benzene ring improved the description of the interaction between the benzene rings.<sup>18</sup> Thus we tentatively introduced the dipoles, which were used by Allinger

\* 1 cal = 4.184 J.

**Table 2.** Deformation of the benzene ring in *para*-cyclophane in terms of angles  $\alpha$  and  $\beta$ .<sup>a</sup>

Molecule		Deformation angles/ $^{\circ}$				
		X-Ray	Symmetry	This work	MMP2 (1982)	MMP2 (1985)
[8]- <i>para</i> -cyclophane (1)	$\alpha$	9.0, 9.2 <sup>b</sup>	$C_2$	8.1	13.3	11.3
	$\beta$	5.2, 5.9		7.4	6.6	4.6
[7]- <i>para</i> -cyclophane (2)	$\alpha$	17 <sup>c</sup>	$C_s$	12.4	18.6	17.6
	$\beta$	6.5		13.2	11.8	7.9
[6]- <i>para</i> -cyclophane (3)	$\alpha$	19.4, 19.5 <sup>d</sup>	$C_2$	15.7	22.7	24.6
	$\beta$	18.6, 21.2		22.5	20.0	12.5
[3.3]- <i>para</i> -cyclophane (4)	$\alpha$	6.1, 6.5 <sup>e</sup>	$C_{2h}$	4.3	6.3	5.6
	$\beta$	5.0, 2.3		2.1	1.5	2.2
[2.2]- <i>para</i> -cyclophane (5)	$\alpha$	12.6 <sup>f</sup>	$D_2$	10.4	14.8	12.9
	$\beta$	11.2		11.1	12.5	12.0

<sup>a</sup> Angles  $\alpha$  and  $\beta$  are defined according to ref. 14. See Figure 2. <sup>b</sup> [8]-*para*-cyclophane-4-carboxylic acid: ref. 15(a). <sup>c</sup> [7]-*para*-cyclophane-3-carboxylic acid: ref. 15(b). <sup>d</sup> [6]-*para*-cyclophane-8,9-dicarboxylic acid: ref. 15(c). <sup>e</sup> Ref. 15(d). <sup>f</sup> Ref. 15(e).

**Table 3.** Out-of-plane deformation of ring and adjacent carbon atoms of [2.2]-*meta*-cyclophane (6) from the plane defined by the C-2, C-3, C-5, and C-6 atoms.

Atom <sup>a</sup>	Distance from mean plane/ $\text{\AA}$			
	Exp. <sup>b</sup>	This work	MMP2 (1982)	MMP2 (1985)
C-1	0.042	0.075	0.078	0.066
C-4	0.143	0.125	0.173	0.173
C-7	0.368	0.359	0.455	0.425

<sup>a</sup> Numbering scheme is shown in Figure 3. <sup>b</sup> Ref. 19.

and Lii,<sup>18b</sup> to our force field and calculated the geometries and energies of compounds (4) and (5) again. Contrary to our expectations, the introduction of the dipoles changed the calculated deformation angles of (4) and (5) by  $<0.2^{\circ}$  and changed the inversion barrier of compound (4) by  $<0.2$  kcal mol<sup>-1</sup>.

The out-of-plane deformation of the benzene rings of [2.2]-*meta*-cyclophane (6) (Figure 3) calculated by our force field is very close to the X-ray value<sup>19</sup> as well as the MMP2(82) and MMP2(85) values as shown in Table 3.

X-Ray crystallography of [2.2]-*para*-cyclo-(4,6)[2.2]-*meta*-*para*-cyclophane (7) and [2.2]-*meta*-cyclo-(4,6)[2.2]-*metapara*-cyclophane (8)<sup>20</sup> has shown that compound (7) takes the *anti*-form and compound (8) has the *syn*-form (Figure 4). These preferences are well reproduced by our force field. *anti*-(7) is 4.3 kcal mol<sup>-1</sup> more stable than *syn*-(7), and *syn*-(8) is 3.8 kcal mol<sup>-1</sup> more stable than *anti*-(8). Whereas the experimental deformation angles of benzene rings are well reproduced by our force field and by MMP2(85) as summarized in Table 4, the deformation angles are overestimated by MMP2(82).

A thermal isomerization study of triple-layered [2.2]-*meta*-cyclophane (9) has shown that this molecule prefers the *syn*- to the *anti*-form by at least 4 kcal mol<sup>-1</sup> in toluene.<sup>21</sup> MINDO/2 calculations of deformed benzenes have indicated that benzene is more stable in the boat than in the chair form, a conclusion that supports the preference of *syn*-(9), wherein the central benzene is a boat conformer.<sup>22</sup> The preference of the *syn*-form of compound (9) is reproduced by our force field. *syn*-(9) is calculated to be 6.6 kcal mol<sup>-1</sup> more stable than *anti*-(9).

The activation energy ( $\Delta H^{\ddagger}$ ) of conformational flipping in [2.2]-*metapara*-cyclophane (10) has been measured as  $17.0 \pm 0.5$  kcal mol<sup>-1</sup> in CDCl<sub>3</sub>.<sup>23</sup> A much higher barrier of 30.6 kcal mol<sup>-1</sup> was obtained by MMP2(85), which imposed  $C_{2v}$

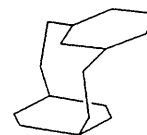
**Table 4.** Deformation angles of [2.2]-*para*-cyclo-(4,6)[2.2]-*metapara*-cyclophane (7) and [2.2]-*meta*-cyclo-(4,6)[2.2]-*metapara*-cyclophane (8).

Deformation angle/ $^{\circ}$	Exp. <sup>b</sup>	This work	MMP2 (1982)	MMP2 (1985)
(7)				
$\alpha$	4.3	2.5	8.2	7.4
(8)				
$\alpha_1$	12.5	12.7	16.8	13.0
$\alpha_2$	14.2	14.4	19.9	17.0
$\alpha_3$	9.5	10.2	14.3	11.8
$\alpha_4$	4.6	6.1	6.4	4.9

<sup>a</sup> Numbering scheme is shown in Figure 4.  $\alpha$  is the angle between the C-2, C-3, C-5, C-6 plane and the C-3, C-4, C-5 plane of compound (7).  $\alpha_1$  is the angle between the C-2, C-3, C-5, C-6 plane and the C-1, C-2, C-6 plane of compound (8).  $\alpha_2$  is the angle between the C-2, C-3, C-5, C-6 plane and the C-3, C-4, C-5 plane of compound (8).  $\alpha_3$  is the angle between the C-8, C-9, C-11, C-12 plane and the C-7, C-8, C-12 plane of compound (8).  $\alpha_4$  is the angle between the C-8, C-9, C-11, C-12 plane and the C-9, C-10, C-11 plane of compound (8). <sup>b</sup> Ref. 20.

symmetry on the saddle-point conformer.<sup>6b</sup> Our force field gave a barrier height of 25.6 kcal mol<sup>-1</sup>. The calculated saddle-point conformer has  $C_2$  symmetry and the energy-minimum conformer has  $C_s$  symmetry.

The deformation angles and conformational energies of cyclophanes calculated by our force field do not agree completely with the experimental values. The  $\beta$  angle of compound (2) is overestimated. The calculated activation energy of compound (10) is larger than the experimental values. The



(10)

reason for these disagreements is not certain. We suspect that the partial refinement of the parameters in this work may be the cause of this deficiency. We refined only a limited number of force constants and torsional parameters. It would be better to refine all the parameters based on *ab initio* calculations. However, the overall performance of our force field is satis-

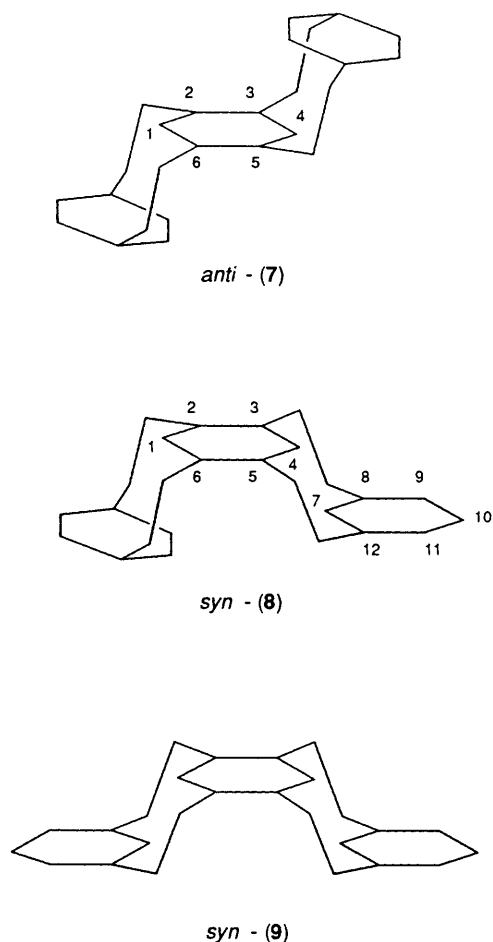


Figure 4. Structures and numbering schemes of triple-layered cyclophanes (7)–(9).

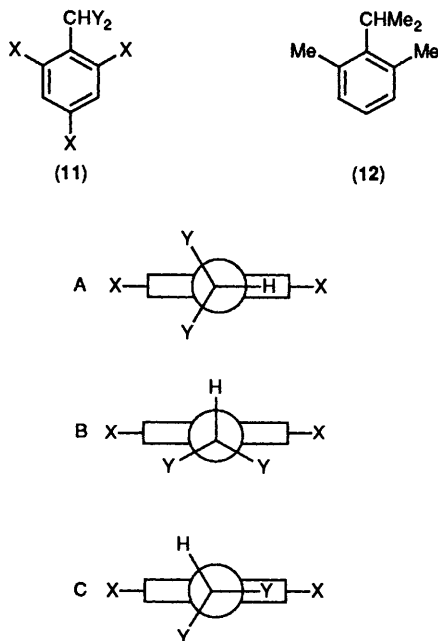


Figure 5. Conformers of substituted isopropylbenzenes (11) and (12)

factory. Our force field reproduces most of the experimental deformation angles and conformational energies as well as those calculated by MMP2(85).

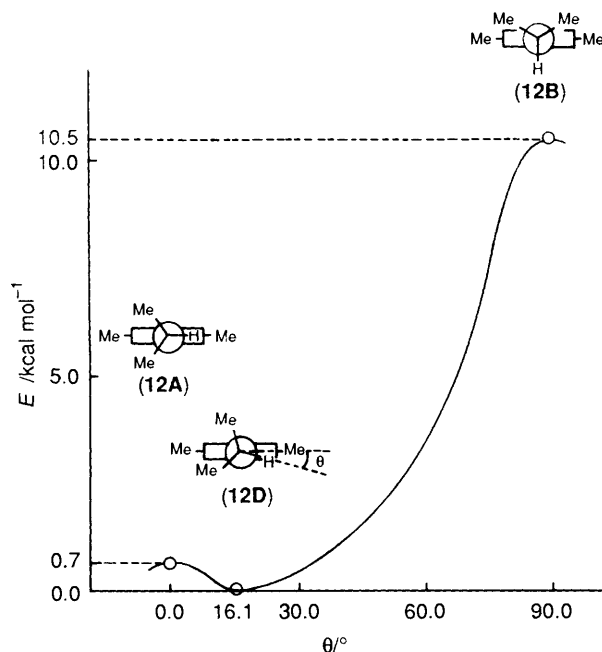


Figure 6. Potential-energy curve of 2-isopropyl-1,3-dimethylbenzene (12) calculated with our force field.

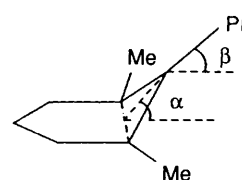


Figure 7. Definition of ring-deformation angles of 2-isopropyl-1,3-dimethylbenzene.

*2-Isopropyl-1,3-dimethylbenzene.*—There is much interest in the structure and dynamics of  $\alpha,\alpha,2,4,6$ -penta substituted toluenes (11)<sup>24</sup> (Figure 5). NMR spectra of compounds (11; X = Y = Cl; X = Br, Y = Cl) at low temperatures showed an ABX pattern, where X was a methine proton, hence structure A, and not B, would be the stable rotational isomer<sup>24a,b</sup> (structure B would have given an A<sub>2</sub>X spectrum). The saddle-point conformer was first expected to have the conformation C, having an eclipsed X–Y interaction.<sup>24a,24b</sup> However, molecular mechanics calculations later indicated that the saddle-point conformer had structure B.<sup>24d,e,25</sup> Two repulsive X–Y interactions in conformer B were calculated to be energetically more costly than the X–Y interaction in conformer C.

According to the calculations with our force field, the energy-minimum structure of 2-isopropyl-1,3-dimethylbenzene (12) does not exactly correspond to conformer (12A), but to an intermediate structure (12D) wherein the isopropyl group is rotated by 16° towards conformer B (Figure 6). Structures (12A) and (12B) turned out to be saddle points, giving barrier heights of 0.7 and 10.5 kcal mol<sup>-1</sup>, respectively, from (12D). The observed ABX NMR pattern of ring protons<sup>24</sup> agrees with the unsymmetrical structure (12D) for the energy minimum.

The internal rotational barrier heights of compound (12) obtained by MMP2(82) and MMP2(85) calculations are 8.6 and 9.7 kcal mol<sup>-1</sup>, respectively. The calculated rotational barrier height with the newly refined parameters is still 1.3 kcal mol<sup>-1</sup> lower than the  $\Delta H^\ddagger$  value deduced from the experimental  $\Delta G^\ddagger$  and  $\Delta S^\ddagger$  values.<sup>7,25</sup> However, this value is closer to the experimental value than are those obtained with MMP2(82) and MMP2(85) calculations.

**Table 5.** Deformations of the benzene ring in the saddle-point conformers of 2-isopropyl-1,3,5-trimethylbenzene (**11**; X = Y = Me), and 2-isopropyl-1,3-dimethylbenzene (**12**).

Angle <sup>a</sup> /°	(12) This work	(11; X = Y = Me)	
		MMP2 <sup>b</sup> (1982)	MMP2 <sup>b</sup> (1985)
C-1-C-2-C-3-C-4	-4.4	-14.5	-14.3
C-t-C-2-C-3-C-Me	-11.2	-24.7	-13.2
α	3.8	13.2	12.5
β	5.0	14.1	9.5

<sup>a</sup> For definition of α and β, see Figure 7. <sup>b</sup> Ref. 7.**Table 6.** Valence angles of 1,2,4,5-tetra-*t*-butylbenzene (**13**)

Angle <sup>a</sup> /°	Exp <sup>b</sup>	This work	MMP2 (1982)	MMP2 (1985)
C-1-C-2-C-3	115.1, 115.4	116.6	113.6	114.0
C-2-C-3-C-4	129.5	125.9	125.0	131.2
C-2-C-1-C-7	129.9, 131.0	128.7	129.3	130.4
C-6-C-1-C-7	113.9, 114.7	114.7	117.0	115.4

<sup>a</sup> Numbering scheme is shown in Figure 8. <sup>b</sup> Ref. 26.**Table 7.** Deviations of ring and quaternary carbon atoms from their best plane of 1,2,4,5-tetra-*t*-butylbenzene (**13**).

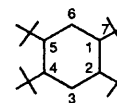
Atom <sup>a</sup>	Distance from mean plane/Å			
	Exp <sup>b</sup>	This work	MMP2 (1982)	MMP2 (1985)
C-1	0.005, 0.011	0.067	0.202	0.065
C-3	0.001	0.000	0.000	0.006
C-7	0.002, 0.005	0.242	0.887	0.183

<sup>a</sup> Numbering scheme is shown in Figure 8. <sup>b</sup> Ref. 26.

The calculated structure of the transition state during the rotation of the C<sub>ar</sub>-C<sub>tert</sub> bond of compound (**12**) calculated by our force field is compared with those of (**11**; X = Y = Me) by MMP2(82) and MMP2(85) methods.<sup>7</sup> Only four key angles are summarized in Table 5. The definition of ring-deformation angles is shown in Figure 7. Deformations calculated by MMP2 are significantly larger than those calculated by our force field. The refinement of the bending-force constants and torsional parameters for benzene makes this ring stiffer to deformation and increases the rotational barrier height.

**1,2,4,5-Tetra-*t*-butylbenzene.**—The molecular structure of 1,2,4,5-tetra-*t*-butylbenzene (**13**) (Figure 8) has been investigated by X-ray crystallography.<sup>26</sup> Steric repulsion between vicinal *t*-butyl groups produces considerable in-plane deformation in the benzene ring (Table 6), but gives only slight out-of-plane deformation (Table 7).

The calculated geometries of compound (**13**) by our force field, MMP2(82), and MMP2(85) methods are compared with the X-ray structure.<sup>26</sup> Whereas our force field and MMP2(85) perform satisfactorily, MMP2(82) gives too large deviations of the ring atoms and quaternary atoms from their best planes (Table 7). This deficiency must be caused by the small *DEs* of the out-of-plane modes given by this force field. The deviations given by our force field are smaller than those by MMP2(82), but they are still larger than the experimental values. The refinement of

**Figure 8.** Numbering of 1,2,4,5-tetra-*t*-butylbenzene (**13**) for Tables 6 and 7.

only a limited number of parameters is a possible reason for the modest performance of our force field with regard to structure (**13**).

**Conclusions.**—A 'mechanical approach' using newly refined in-plane angle bending-force constants and torsional parameters for the C<sub>ar</sub>-C<sub>ar</sub> bond based on the deformation energies of the benzene ring obtained by *ab initio* calculations shows good performance in the calculations of the geometries of cyclophanes and 1,2,4,5-tetra-*t*-butylbenzene, and in the calculations of the internal rotational barrier height of 2-isopropyl-1,3-dimethylbenzene; the results are as good as those obtained by MMP2(85).

### Acknowledgements

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