

# Novel Method for Geometry Optimization of Molecular Clusters: Application to Benzene Clusters

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A heuristic and unbiased method for searching optimal geometries of clusters of nonspherical molecules was constructed from the algorithm recently proposed for Lennard-Jones atomic clusters. In the method, global minima are searched by using three operators, interior, surface, and orientation operators. The first operator gives a perturbation on a cluster configuration by moving molecules near the center of mass of a cluster, and the second one modifies a cluster configuration by moving molecules to the most stable positions on the surface of a cluster. The moved molecules are selected by employing a contribution of the molecules to the potential energy of a cluster. The third operator randomly changes the orientations of all molecules. The proposed method was applied to benzene clusters. It was possible to find new global minima for (C<sub>6</sub>H<sub>6</sub>)<sub>11</sub>, (C<sub>6</sub>H<sub>6</sub>)<sub>14</sub>, and (C<sub>6</sub>H<sub>6</sub>)<sub>15</sub>. Global minima for (C<sub>6</sub>H<sub>6</sub>)<sub>16</sub> to (C<sub>6</sub>H<sub>6</sub>)<sub>30</sub> are first reported in this article.

## INTRODUCTION

A heuristic and unbiased method for the geometry optimization of Lennard-Jones (LJ) atomic clusters has recently been proposed by the present author.<sup>1</sup> In the method, two novel operators modify a cluster configuration. The modified geometry is locally optimized by using a limited-memory quasi-Newton method (L-BFGS<sup>2</sup>). This is repeated if the potential energy of a cluster is improved. The proposed method yielded putative global minima for LJ<sub>10</sub> to LJ<sub>561</sub> reported in the literature<sup>3–11</sup> with reducing computational effort compared with previous unbiased methods.<sup>1</sup> Moreover, it was possible to find new global minima for LJ<sub>506</sub>, LJ<sub>521</sub>, LJ<sub>536</sub>, LJ<sub>537</sub>, LJ<sub>538</sub>, and LJ<sub>541</sub>. Therefore, the method was proved to be clever and efficient for the geometry optimization of comparatively large LJ atomic clusters.

In the present study, the above method is modified to treat a more complicated problem, the geometry optimization of clusters of nonspherical molecules. To illustrate the performance of the modified method, geometries of benzene clusters up to 30 molecules are optimized.

## BENZENE CLUSTERS

Many investigations on benzene clusters were reported.<sup>12–24</sup> A theoretical investigation on optimal structures of benzene clusters was initiated by Williams<sup>23</sup> with the potential of Williams and Starr.<sup>25</sup> The same potential is used throughout the present study since it was used by Pullan,<sup>19</sup> White et al.,<sup>20</sup> Easter,<sup>21,22</sup> and van de Waal.<sup>24</sup> The molecular structure of benzene is assumed to be rigid and to take *D*<sub>6h</sub> symmetry with a C–C bond length of 1.397 Å and a C–H bond length of 1.027 Å.<sup>23</sup> In this model, the potential energy of a cluster of *n* molecules (C<sub>6</sub>H<sub>6</sub>)<sub>*n*</sub> takes the form

$$V = \sum_{i=1}^{n-1} \sum_{j=i+1}^n V(i,j) = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \sum_{k=1}^{12} \sum_{l=1}^{12} \left[ B_{kl} \exp(-C_{kl} r_{ij}^{kl}) - \frac{A_{kl}}{(r_{ij}^{kl})^6} + \frac{q_k q_l}{r_{ij}^{kl}} \right] \quad (1)$$

Here, *V*(*i,j*) is the potential energy between *i*th and *j*th molecules, *k* and *l* represent the numbering of atoms in the two molecules *i* and *j*, respectively, and *r*<sub>*ij*</sub><sup>*kl*</sup> denotes the distance between the two atoms *k* and *l*. The potential parameters *A*, *B*, *C*, and *q* are reported in ref 25.

Williams<sup>23</sup> predicted configurations of clusters of 2, 3, 5, 7, 9, 11, 13, and 15 molecules under the assumption that a center of symmetry is present in all clusters except the dimer. The configurations of trimer, pentamer, and heptamer in ref 23 were subsequently improved by van de Waal.<sup>24</sup> By using real-coded genetic algorithms (GAs), Pullan<sup>19</sup> and White et al.<sup>20</sup> found the putative global minima for clusters up to 15 molecules and up to 13 molecules, respectively. Isomers of the 13-molecule cluster were investigated with several potential energy functions by Monte Carlo simulations.<sup>21,22</sup> The energies obtained in these investigations are listed in Table 1.

## OPTIMIZATION METHOD

The method proposed in this article is based on the algorithm obtained in the study on LJ atomic clusters.<sup>1</sup> In the algorithm, a geometry randomly generated is locally optimized by using the L-BFGS<sup>2</sup> method. The resulting geometry is modified by using the surface and interior operators: one modifies a cluster configuration by moving atoms to the most stable positions on the surface of a cluster, and the other gives a perturbation on a cluster configuration by moving atoms near the center of mass of a cluster. The highest-energy group of atoms is generally selected as the group of moved atoms.

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**Table 1.** Lowest-Energy Values of Benzene Clusters (C<sub>6</sub>H<sub>6</sub>)<sub>n</sub> Obtained in the Present Study and the Literature (in kJ mol<sup>-1</sup>)

<i>n</i>	Williams <sup>23</sup>	van de Waal <sup>24</sup>	Easter <sup>21,22</sup>	Pullan <sup>19</sup>	White et al. <sup>20</sup>	this work
2	-11.0	-11.0		-11.0	-11.0	
3	-22.1	-32.1		-32.1	-32.1	
4		-55.6		-55.6	-55.6	-55.6
5	-65.7	-79.1		-79.1	-79.1	-79.1
6		-106.1		-106.4	-106.5	-106.5
7	-114.8	-134.1		-134.1	-134.1	-134.1
8				-161.4	-161.7	-161.7
9	-161.0			-190.8	-191.5	-191.5
10				-221.5	-221.5	-221.5
11	-237.6			-251.8	-252.2	-253.6
12				-286.3	-286.3	-286.3
13	-325.3		-325.3	-324.6	-324.7	-325.3
14				-347.5		-356.0
15	-372.3			-371.3		-388.9

In the present study, these operators are modified to treat molecular clusters. In addition, an operator changing orientations of molecules (orientation operator) is introduced into the algorithm. Therefore, the interior, surface, and orientation operators are used for exploring the search space in optimization. The details of these operators and the optimization algorithm are described below.

**Interior Operator  $I_m$ .** This operator moves the  $m$  molecules with the highest energy to the interior of a cluster as follows: (i) Create a list of molecules on the outer shell of the cluster. (ii) For all the combinations of  $m$  molecules in the list (numbering of molecules is represented by  $k_1, k_2, \dots, k_m$ ), calculate the contribution  $V_{\text{select}}(k_1, k_2, \dots, k_m)$  of these molecules to the energy of the cluster by using a formula such as

$$V_{\text{select}}(k_1, k_2, \dots, k_m) = \sum_{i=1}^m V(k_i) - \sum_{i=1}^{m-1} \sum_{j=i+1}^m V(k_i, k_j) \quad (2)$$

Here,  $V(k_i)$  denotes the energy of  $k_i$ th molecule and is calculated from the equation

$$V(k_i) = \sum_{j \neq k_i}^n V(k_i, j) \quad (3)$$

In this step,  $n_o C_m$  evaluations of  $V_{\text{select}}$  are performed where  $n_o$  denotes the number of the outer molecules in the list. (iii) From all the evaluations, select the  $m$  molecules with the highest energy. (iv) Find the molecule which is the closest to the center of mass of the cluster (the central molecule). (v) The positions (the centers of mass) of the molecules selected in step iii are moved on the spherical surface with the radius  $r_e/2$ , where  $r_e$  denotes the distance between equilibrium positions of two molecules.<sup>26</sup> The center of the sphere coincides with the center of mass of the central molecule.<sup>27</sup> Orientations (Euler angles) of the moved molecules are randomly determined.

In general, the number of molecules surrounding the moved molecules increases compared with that surrounding the molecules at the previous instant. Therefore, the potential energy of the moved molecules obtained after local optimization is considered to be lower than the previous energy of the molecules. This leads to the expectation that the potential energies of clusters are improved by using the  $I_m$  operator.

**Surface Operator  $S_m$ .** The highest-energy group of molecules is moved on the surface of a cluster. The most

stable set of positions on the surface is selected as the positions of the moved molecules. The procedure used in this operator is as follows: (i) Remove the  $m$  molecules with the highest energy from the cluster, and prepare the template cluster composed of the  $(n - m)$  molecules. (ii) Add a molecule on the surface of the template cluster at random, and optimize the position and orientation of the added molecule. The space  $S$  occupied by the molecule (described in terms of its position and orientation) and the potential energy between the molecule and the template  $V_{\text{template}}(S)$  are stored. This is repeated  $3n$  times to create a list of distinct spaces.<sup>28</sup> (iii) Calculate the energy  $V_{\text{surface}}$  for all the combinations of  $m$  spaces in the list by

$$V_{\text{surface}}(S_1, S_2, \dots, S_m) = \sum_{i=1}^m V_{\text{template}}(S_i) + \sum_{i=1}^{m-1} \sum_{j=i+1}^m V(S_i, S_j) \quad (4)$$

where  $m$  spaces are represented by  $S_1, S_2, \dots, S_m$  and  $V_{\text{template}}(S_i)$  is obtained in step ii. (iv) Search the combination with the lowest potential energy  $V_{\text{surface}}^{\text{min}}$  from all the combinations. If the combination corresponds to the spaces occupied by the molecules removed in step i, the combination is not taken into account. (v) When  $m \geq 2$ ,<sup>29</sup> for all the configurations with the energy less than  $V_{\text{surface}}^{\text{min}} + 5.0$  kJ mol<sup>-1</sup>, the positions and orientations of  $m$  molecules are simultaneously optimized. (vi) The positions and orientations giving the lowest energy are used for the moved molecules.

The surface operator for the highest-energy molecule is similar to the directed mutation operator proposed by Hartke;<sup>30</sup> in his study on LJ clusters, the highest-energy atom is moved to the best vacancy position. The surface operator for the highest-energy group of some molecules is considered as an extension of the directed mutation operator.

The number of moved molecules  $m$  limits the search space in optimization. In the present study, the condition used for atomic LJ clusters<sup>1</sup> was adopted without any change:  $m \leq 4$  for the surface operator and  $m \leq 5$  for the interior operator.

**Orientation Operator.** Different isomers may be created from a current configuration by changing orientations of molecules and then by optimizing the resulting geometry. Therefore, the orientation operator randomizes Euler angles of all molecules in a cluster. This kind of modification does not occur in the geometrical perturbation caused by the interior and surface operators. Modification of the orientational degrees of freedom in molecular clusters was used in

previous optimization methods on water clusters by Wales and Hodges,<sup>31</sup> Niesse and Mayne,<sup>32</sup> and Bandow and Hartke.<sup>33</sup>

**Optimization Algorithm.** The following steps are performed in the present study:

(1) To create an initial geometry, molecules are randomly placed in a sphere having a radius of  $R = (3n/4\pi)^{1/3}r_e$ .<sup>1</sup> The geometry is locally optimized by the L-BFGS method.<sup>2</sup>

(2) A new geometry is created from a current geometry by using the  $I_m$  operator where  $m$  is randomly chosen from 1–5.<sup>1</sup> The resulting geometry is optimized by the L-BFGS method.

(3) If the potential energy is not lowered by using the  $I_m$  operator during the last 10 optimizations, go to the next step. Otherwise, update the cluster geometry if the potential energy is improved and return to step 2.

(4) The lowest-energy geometry obtained in previous steps is modified by using the  $S_m$  operator, and the local optimization of the modified geometry is carried out. The value of  $m$  is initially 1 and increases up to 4 at an interval of 1 if the energy of the cluster is not improved.<sup>1</sup> In the case of the  $S_1$  operator, if the energy of the cluster is not improved by moving the highest-energy molecule, the second highest-energy molecule and the third highest-energy molecule are separately moved. This improves the performance of the present method and is not carried out in the directed mutation<sup>30</sup> operator. When energy lowering is observed, initialize the  $m$  value, update the cluster geometry, and repeat this step.

(5) If the  $S_4$  operator does not improve the energy of the cluster, the orientation operator is carried out and the resulting geometry is optimized by L-BFGS method.

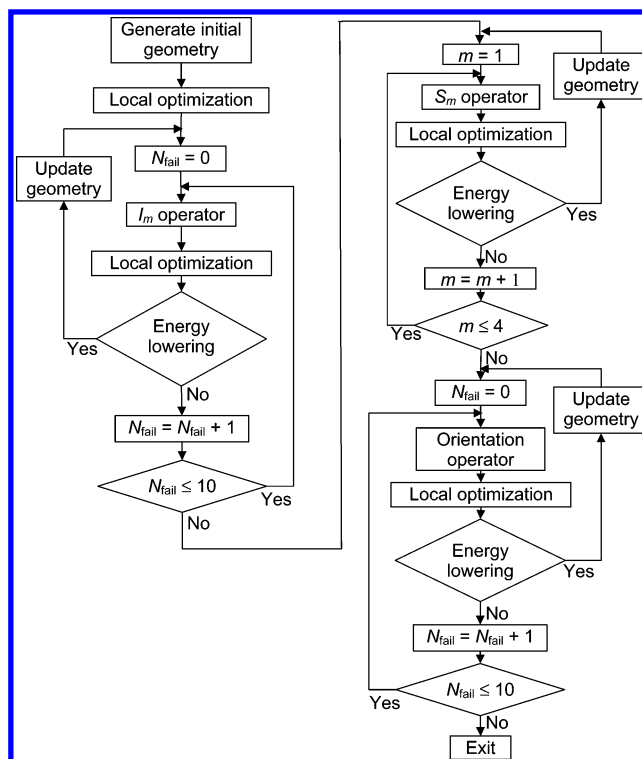
(6) If the orientation operator does not lower the energy of the cluster during the last 10 optimizations, we terminate the calculation. The algorithm proposed in the present study is summarized in Figure 1.

In the above algorithm, the interior operator is performed prior to the surface operator. In calculations where the order of the two operators was reversed, the efficiency of the algorithm was found to be very low for large LJ clusters. For example, the number of local optimizations required for obtaining the global minimum of LJ<sub>200</sub> is 25 600, a value which is approximately 10 times larger than that reported in ref 1, 2371. Therefore, geometry optimization of molecular clusters as well as LJ clusters was carried out by the above algorithm.

The cycle shown in Figure 1 was repeated in the geometry optimization of benzene clusters in the range of  $4 \leq n \leq 30$ . For small clusters with  $n = 4$ –7, the number of moved atoms in the  $I_m$  and  $S_m$  operators was set at  $n - 3$ .<sup>34</sup> Table 2 lists the number of cycles performed for each cluster and the number of the cycles where the same lowest energy is obtained. The program was written in FORTRAN,<sup>35</sup> and one cycle for each cluster of 10, 20, and 30 molecules took approximately 0.3, 3, and 5 min, respectively, on a 2.2 GHz Pentium IV processor.

## RESULTS AND DISCUSSION

Tables 1 and 3 list the lowest-energy values obtained in the present study. The 11-molecule cluster calculated in the present study is more stable than the clusters previously



**Figure 1.** Flowchart for an optimization cycle proposed for molecular clusters.

**Table 2.** Number of Cycles ( $N$ ) Performed in the Geometry Optimization of  $(C_6H_6)_n$  and the Number of Cycles ( $N_s$ ) Where the Lowest-Energy Isomer Is Searched

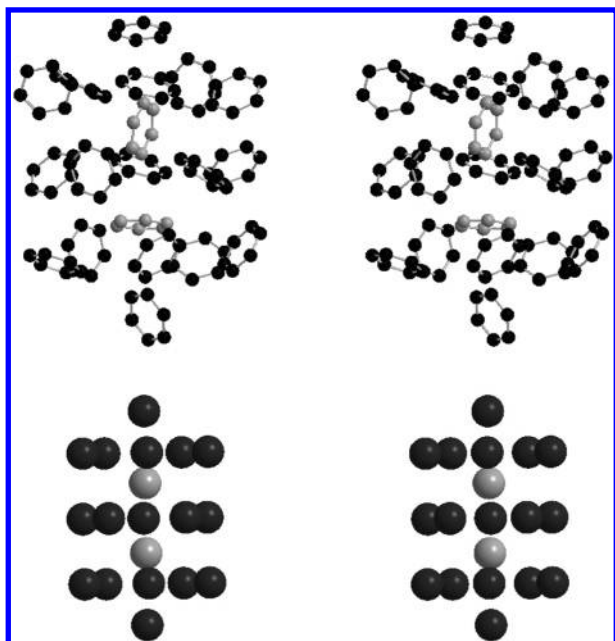
$n$	$N$	$N_s$	$n$	$N$	$N_s$	$n$	$N$	$N_s$
4	10	10	13	200	136	22	1800	7
5	10	10	14	200	127	23	400	27
6	10	9	15	200	55	24	1800	9
7	10	9	16	200	34	25	1800	21
8	10	8	17	200	13	26	800	13
9	100	25	18	200	17	27	1200	8
10	200	21	19	200	37	28	3500	6
11	200	28	20	200	47	29	5000	11
12	200	61	21	200	16	30	7000	5

**Table 3.** Putative Global-Minimum Energies of Benzene Clusters for  $n > 15$  (in  $\text{kJ mol}^{-1}$ )

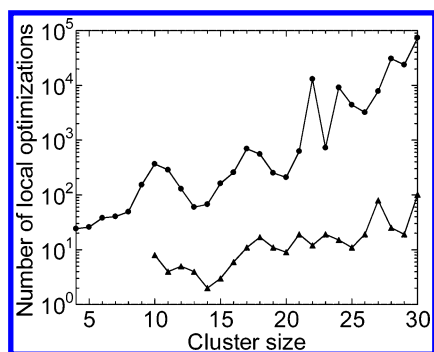
$n$	energy	$n$	energy	$n$	energy	$n$	energy	$n$	energy
16	-421.6	19	-526.4	22	-627.9	25	-736.4	28	-845.4
17	-454.6	20	-561.4	23	-666.9	26	-772.7	29	-882.0
18	-488.3	21	-593.7	24	-700.9	27	-808.1	30	-921.3

reported<sup>19,20,23</sup> by at least  $1.4 \text{ kJ mol}^{-1}$  in energy. The energies of  $(C_6H_6)_{14}$  and  $(C_6H_6)_{15}$  obtained in the present study are significantly lower than those reported in refs 19 and 23. The present study locates the putative global minima of clusters up to 30 molecules as shown in Table 3.

Pullan<sup>19</sup> and White et al.<sup>20</sup> failed to find the global minimum of the 13-molecule cluster. Easter<sup>21</sup> confirmed that the global-minimum energy is  $-325.3 \text{ kJ mol}^{-1}$ . However, the second lowest-energy cluster with an energy of  $-324.7 \text{ kJ mol}^{-1}$  was not found in ref 21. The cluster was found in the subsequent study<sup>22</sup> by referring to the result obtained with the potential different from that of Williams and Starr.<sup>25</sup> In the present method, 136 out of 200 cycles yielded the lowest-energy configuration (see Table 2), and the second lowest-energy isomer was also found in 114 cycles. The present



**Figure 2.** Stereographic views of the lowest-energy configurations of  $(\text{C}_6\text{H}_6)_{19}$  (upper) and  $\text{LJ}_{19}$  (lower). Two interior molecules in  $(\text{C}_6\text{H}_6)_{19}$  and the corresponding atoms in  $\text{LJ}_{19}$  are drawn as gray-colored ones. The two interior molecules are distinct in  $(\text{C}_6\text{H}_6)_{19}$ , whereas there are two identical interior atoms in  $\text{LJ}_{19}$ .



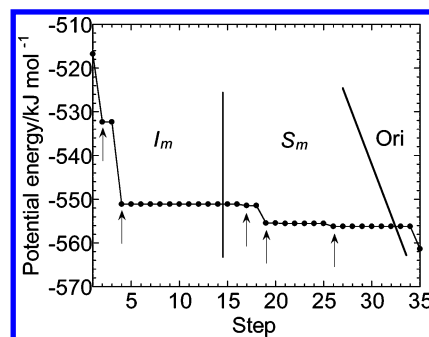
**Figure 3.** Number of local optimizations for benzene clusters (circles) and LJ clusters (triangles) versus the cluster size (the number of molecules or atoms).

method identifies many low-energy isomers in a cycle. It was found that the second lowest-energy isomer of  $(\text{C}_6\text{H}_6)_{13}$  could be obtained from the lowest-energy isomer by using the orientational operator.

According to the GA used by White et al.,<sup>20</sup> the probability that the global minimum of  $(\text{C}_6\text{H}_6)_9$  is obtained within  $3 \times 10^5$  local optimizations is 0.4. In the present study, the average number and maximum number of local optimizations needed for global optimization of the same cluster are 153 and 545, respectively. The above discussion shows that the present method is more efficient than the methods used in the literature.

Figure 2 shows the lowest-energy configuration of  $(\text{C}_6\text{H}_6)_{19}$  with that of  $\text{LJ}_{19}$ . In the assignments of two-photon ionization spectra, Easter and co-workers assumed that two interior molecules in  $(\text{C}_6\text{H}_6)_{19}$  are identical by referring to the  $\text{LJ}_{19}$  cluster.<sup>14</sup> However, the assumption is not valid, as shown in Figure 2. This suggests that the assignments reported in ref 14 should be revised.

Figure 3 shows the average number of local optimizations required for global optimization of each benzene cluster.



**Figure 4.** Energy variation in the geometry optimization of  $(\text{C}_6\text{H}_6)_{20}$ . The  $I_m$  operator is performed until the 14th step, and the orientation operator (represented by Ori) starts at the 33rd step. The last 10 (36th–45th) steps with the orientation operator are omitted in this figure. The energy-lowering is observed at the 2nd, 4th, 17th, 19th, 26th, and 35th steps. At the 17th, 19th, and 26th steps, the  $S_m$  operator moves the third highest-energy molecule, the second highest-energy molecule, and the highest-energy group of four molecules, respectively.

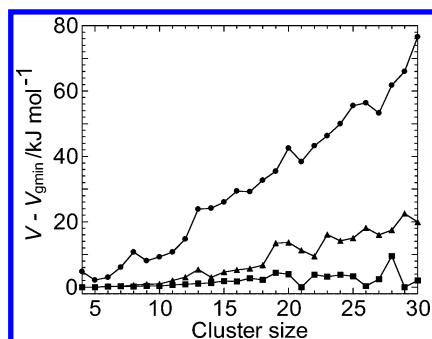
Although the number of independent geometrical parameters of  $(\text{C}_6\text{H}_6)_{10}$  is equal to that of  $\text{LJ}_{20}$ , the number of local optimizations for  $(\text{C}_6\text{H}_6)_{10}$  is 1 order of magnitude larger than that for  $\text{LJ}_{20}$ . The number of local optimizations for  $\text{LJ}_n$  with  $n < 350$ <sup>1</sup> is smaller than that for  $(\text{C}_6\text{H}_6)_{30}$ ,  $7.4 \times 10^4$ . Therefore, the global optimization of benzene clusters is much more difficult than that of LJ clusters. Similar difficulty is observed for benzene clusters by White et al.,<sup>20</sup> and for water clusters by Bandow and Hartke,<sup>33</sup> Wales and Hodges,<sup>31</sup> and James et al.<sup>36</sup> The difficulty is considered to originate from the interaction between translational and orientational degrees of freedom existing in molecular clusters.

Figure 4 shows energy variation in the cycle which locates the global-minimum configuration of  $(\text{C}_6\text{H}_6)_{20}$ . The  $I_m$  operator reduces the energy of the cluster from  $-516.8$  to  $-551.1$   $\text{kJ mol}^{-1}$ . The orientation operator yields the global minimum from the local minimum with an energy of  $-556.2$   $\text{kJ mol}^{-1}$ . This example shows that the  $I_m$  operator significantly decreases the energy of the cluster. Moreover, it is found that the extension of the directed mutation<sup>30</sup> operator, that is, the use of the second highest-energy molecule, the third highest-energy molecule, and the highest-energy group, is efficient for geometry optimization of the benzene clusters.

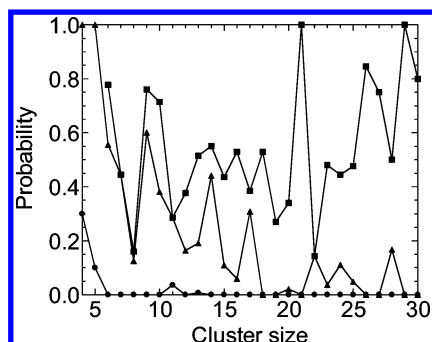
In every cycle, the last 10 geometries are created from a geometry by using the orientation operator and the L-BFGS method.<sup>2</sup> The number of distinct isomers obtained in the last 10 steps was found to be nine for a relatively small cluster with  $n = 10$ . This indicates that the number of local minima on the energy surface of the benzene cluster is larger than that on the surface of the corresponding LJ cluster, in accordance with the above discussion on the difficulty accompanied with the global optimization of benzene clusters.

To examine the performance of the three operators, the energies of initial clusters (obtained in step 1) and the lowest energies of clusters optimized by using the  $I_m$  and  $S_m$  operations (obtained in steps 3 and 4) were averaged over all of the successful cycles. The results are shown in Figure 5. The differences between initial energies and the global-minimum energies ( $V_{\text{gmin}}$ ) are approximately proportional to the cluster size. The energy differences  $V - V_{\text{gmin}}$  are significantly reduced by the  $I_m$  operator and are furthermore decreased by the  $S_m$  operator.





**Figure 5.** Differences of energies of initial geometries (circles) and those of geometries optimized by using the  $I_m$  (triangles) and  $S_m$  (squares) operators from the global-minimum energies  $V_{\text{gmin}}$ .



**Figure 6.** Probabilities that global minima were found at local optimizations of initial geometries (circles) and at local optimizations of geometries modified by using the  $I_m$  (triangles) and  $S_m$  (squares) operators.

Figure 6 shows that initial geometries or geometries modified by using the  $I_m$  operator converge to the lowest-energy configurations in all the successful cycles for  $n = 4$  and 5 and that the  $S_m$  operator locates the global minima in all the successful cycles for  $n = 21$  and 29. For the clusters with  $n > 5$ , the probability that the global minima are obtained is 0.41 before using the orientation operator, and the orientation operator yields the global minima with the remaining probability of 0.59. Therefore, the orientation operator increases the efficiency of the present method at the final stage of the optimization procedure.

## CONCLUSION

The heuristic method based on the three operators is proposed for searching optimal geometries of nonspherical-molecule clusters. The method improves global minima for  $(\text{C}_6\text{H}_6)_{11}$ ,  $(\text{C}_6\text{H}_6)_{14}$ , and  $(\text{C}_6\text{H}_6)_{15}$  and yields new global minima for benzene clusters for  $16 \leq n \leq 30$ . Comparison of the obtained results with the results in the literature clearly shows that the present method is clever and efficient for the geometry optimization of benzene clusters. Therefore, it is expected that the method is successfully applied to relatively small molecular clusters.

The geometry modification performed by using the  $I_m$  and  $S_m$  operators is excellent for lowering potential energies of benzene clusters. The orientation operator is important for searching global minima at the final stage of optimization. Therefore, the combined use of the three operators is essential to the performance of the present method.

## ACKNOWLEDGMENT

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**Supporting Information Available:** The Cartesian coordinates and stereographic views of putative global minima of benzene clusters. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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