Ab Initio Calculations of Intermolecular Interaction Potentials of Corannulene Dimer

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The intermolecular interaction potential of the corannulene dimer in a parallel (D_{5h}) orientation was calculated by ab initio methods using basis sets up to 6-311G(2d) quality, with MP2 level electron correlation energy correction. The calculated potentials have their minima at a separation between the two five-membered rings of 3.2 Å. An interaction energy of −13.39 kcal mol^{-1} was calculated at the MP2/6-311G(2d) level. The calculated electron correlation energy is −24.25 kcal mol^{-1}, indicating that the dispersion interaction is the dominant term in the interaction of the corannulene dimer. The calculated potential in the repulsive region is less steep than those obtained from the Lennard-Jones type atom−atom potential parameters commonly used for the MD simulations of C60. It is suggested that the intermolecular interaction potential derived from the corranulene dimer will outperform atom−atom potentials for molecular dynamics studies of the bulk properties of fullerenes.

Introduction

Properties of condensed-phase fullerenes have attracted much interest, since the preparation of C60 in macroscopic quantities was reported in 1990.[1] The nonbonding interaction of fullerene controls structures and properties of fullerene in the condensed phase.[2] Accurate nonbonding potentials for fullerenes are requested by those who carry out MD simulations of condensed-phase fullerenes. However, it is difficult to confirm the details of the shape of the intermolecular interaction potential of a fullerene only from limited experimental measurements. Due to this reason, the atom−atom potentials from experimental measurements of graphite[3,4] have widely been used for the simulations of C60.[5,6]

Ab initio molecular orbital calculations have been recognized as a powerful method to study intermolecular interaction potentials of organic molecules.[7] It has been reported that ab initio calculations can accurately evaluate intermolecular interactions of small molecules, if a reasonably large basis set is used and if electron correlation and basis set superposition error are treated properly.[8−10] Thus, high-level ab initio calculations could be useful to improve our understanding of the interaction between fullerene molecules. However, the accurate evaluation of the intermolecular interactions including the dispersion interactions requires electron correlation correction and a large basis set with polarization functions. Unfortunately, such level calculations of fullerene dimer are still beyond the capacity of present computers. The benzene[11−13] and toluene dimers[14] were the largest systems that have ever been studied by ab initio calculations using large basis sets including polarization functions and with electron correlation correction.

In this paper we report on the ab initio calculations of the intermolecular interaction potential of the corannulene (C20) dimer as a model of the nonbonding interaction of the fullerene dimer, using large basis sets with polarization functions and with electron correlation correction. In principle, we should have studied the interactions of several orientations of the corannulene dimer. However, the corannulene dimer is a very large system, and it is difficult for present day computers to carry out high-level ab initio molecular orbital calculations of the dimers up to 980 basis functions and 1540 primitive Gaussians. We feel, however, that this approximation made is not critical for the final result.

Computational Method

The Gaussian 94 program[15] was used for ab initio molecular orbital calculations of the dimers. The basis sets implemented in the program were used for calculations.[16−18] The geometry of the corannulene monomer was optimized at the HF/6-31G* level. This geometry was used for the calculations of D_{5h} dimer shown in Figure 1. Electron correlation energies were corrected by the second-order Mϕller−Plesset (MP2) method.[19,20] It has been reported that the MP2 interaction energies of small hydrocarbon molecules are close to the MP4 energies.[12,21−23] The basis set superposition error[24] was corrected by the counterpoise method.[25] Atomic charge distributions of monomer corannulene were obtained by electrostatic potential fitting using the Merz−Singh−Kollman scheme.[26,27] The electrostatic interaction was calculated using the Orient program.[28] The hydrogen/hydrogen Lennard-Jones (12−6) type[29] nonbonding interaction parameters (A = 18.87 kcal mol^{-1} Å^{-6} and B = 44 359 kcal mol^{-1} Å^{-12}) were used for the force field calculations of the corannulene dimers.[30] The parameters for carbon/hydrogen interaction were obtained by the geometrical mean of the corresponding parameters for carbon/carbon and hydrogen/hydrogen interactions.

Results and Discussion

In the parallel structure, the corannulene dimer was found to have an equilibrium separation of 3.2 Å between two five-membered rings, as shown in Figure 1 and Table 1. The depth of the potential greatly depends on the basis set used. The calculated interaction energies with the 6-31G*, 6-311G*, 6-311G**, and 6-311G(2d) basis sets are −8.56, −11.48, −11.86, and −13.39 kcal mol^{-1}, respectively.

Positive SCF interaction energies were obtained for all ring separations, suggesting that the sums of the electrostatic and

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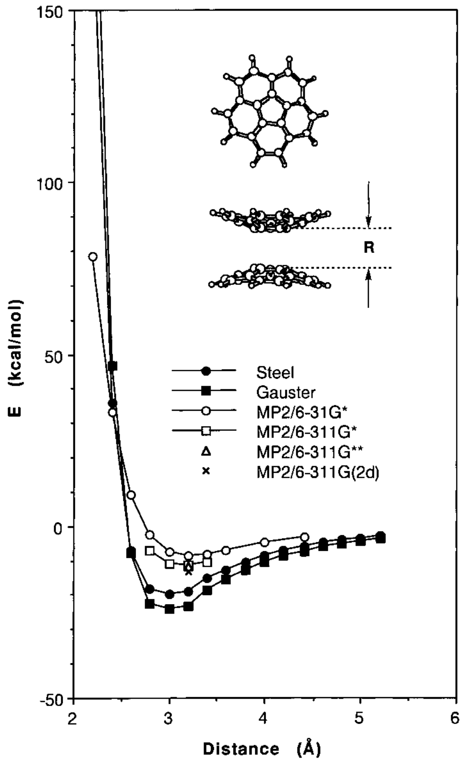

Figure 1. Calculated intermolecular interaction potentials of the D_{5h} corannulene dimer by the ab initio molecular orbital method and by atom−atom potentials.

TABLE 1: Calculated Interaction Energies of the Corannulene Dimer[a]

	energy			
distance (Å)	E_{MP2}[b]	BSSE[c]	E_{HF}[d]	E_{corr}[e]
6-31G*				
2.2	78.45 (53.49)	24.96	156.54	−78.09
2.4	33.21 (13.92)	19.29	91.82	−58.61
2.6	9.22 (−5.39)	14.61	53.48	−44.26
2.8	−2.43 (−13.29)	10.86	31.12	−33.54
3.0	−7.26 (−15.22)	7.96	18.24	−25.50
3.2	−8.56 (−14.32)	5.76	10.89	−19.45
3.4	−8.19 (−12.32)	4.13	6.71	−14.90
3.6	−7.17 (−10.09)	2.92	4.31	−11.48
4.0	−4.89 (−6.24)	1.35	2.09	−6.98
4.4	−3.14 (−3.65)	0.51	1.29	−4.43
6-311G*				
2.8	−7.21 (−18.45)	11.24	30.87	−38.08
3.0	−10.99 (−19.27)	8.28	18.11	−29.11
3.2	−11.48 (−17.44)	5.96	10.86	−22.35
3.4	−10.47 (−14.66)	4.19	6.77	−17.24
6-311G**				
3.2	−11.86 (−17.74)	5.88	10.80	−22.66
6-311G(2d)				
3.2	−13.39 (−20.60)	7.21	10.86	−24.25

[a] Energies in kcal mol^{-1}. [b] Calculated at the MP2 level. The values in parentheses correspond to the energies not corrected for BSSE. [c] The BSSEs calculated at the MP2 level. [d] Calculated at the HF level with BSSE correction. [e] Calculated correlation energies.

TABLE 2: Calculated Polarizability of the Corannulene Monomer with Several Basis Sets[a]

	polarizability	
basis set	α_{xx}, α_{yy}	α_{zz}
6-31G*	243.2	70.5
6-311G*	252.3	84.3
6-311G**	253.2	85.7
6-311G(2d)	256.8	90.5

[a] In au units.

exchange-repulsion interactions are repulsive for all these separations. Similarly, positive SCF interaction energies have also been observed for all ring separations of the parallel (D_{6h}) benzene dimer.[11−13] The basis set effects on the calculated SCF interaction energies are not large. The calculated SCF energies at the separation of 3.2 Å with the 6-31G*, 6-311G*, 6-311G**, and 6-311G(2d) basis sets are 10.89, 10.86, 10.80, and 10.86 kcal mol^{-1}, respectively. The correlation energy, corresponding to the difference between the MP2 and SCF energies, is essentially the attractive dispersion energy arising from the stacking of two aromatic molecules. The choice of the basis set largely affects the calculated correlation energies. The correlation energies at the separation of 3.2 Å calculated with the 6-31G*, 6-311G*, 6-311G**, and 6-311G(2d) basis sets are −19.45, −22.35, −22.66, and −24.25 kcal mol^{-1}, respectively. As expected, the small 6-31G* basis set underestimates the correlation energy. The underestimation of the correlation energies by the use of small basis sets has also been observed in the calculations for dimers of small hydrocarbon molecules.[11−13,21−23] The dispersion energy is approximately proportional to the square of the polarizability. Thus, we summarized the calculated polarizabilities of corannulene in Table 2. The 6-31G* basis set considerably underestimates the polarizability, and this would be the cause of the underestimation of the attractive dispersion interaction with this basis set.

The correlation energy calculated with the 6-311G* basis set is 15% larger than the 6-31G* correlation energy. The addition of the polarization functions on hydrogen atoms over the 6-311G* basis set little affects the calculated correlation energy (less than 2%). On the other hand, the addition of the second d functions on carbon atoms increases the calculated correlation energy of the corannulene dimer by as much as 9%. The basis set effects on the calculated correlation energy of parallel benzene dimer have been reported.[12] The calculated correlation energy of the benzene dimer at the optimal separation of 3.8 Å using the 6-311G* basis set is 19% larger than the 6-31G* correlation energy. The 6-311(2d,p) correlation energy is 13% larger than the 6-311G** correlation energy. These results suggest that the choice of the basis set gives larger effects on the calculated correlation energy of the benzene dimer compared with that of the corannulene dimer.

Further augmentations of polarization functions on carbon atoms over the 6-311G(2d) basis set may change the calculated correlation energy. However, the basis sets larger than the 6-311G(2d) basis set are too large to be employed for the calculations of corannulene dimer. The correlation energy of the parallel benzene dimer calculated with the 6-311G** basis set at the separation of 3.8 Å is −5.76 kcal/mol. Further improvement of the basis set increases the calculated correlation energy. The calculated correlation energy converges by the improvement of the basis set. It appears that the correlation energy is close to −7.3 kcal/mol at the basis set limit. This result suggests that the 6-311G** basis set about 21% underestimates the correlation energy of parallel benzene dimer. The basis set effect on the correlation energy of corannulene dimer would be smaller than that of the benzene dimer. Therefore, we assume that the 6-311G** basis set underestimates the correlation energy of the corannulene dimer by as much as 10−15%. The calculated correlation energy of the corannulene dimer with the 6-311G** basis set is −22.66 kcal mol^{-1}. The correlation energy of corannulene dimer at the basis set limit would be −25.92 ± 0.74 kcal mol^{-1}, if the 6-311G** calculation underestimates the correlation energy by 10−15%. This

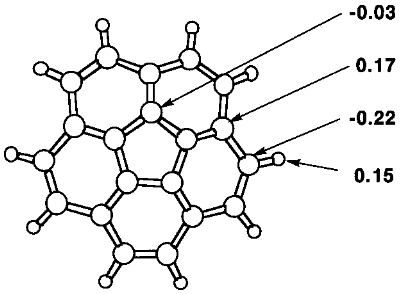

Figure 2. Calculated atomic charge distributions by electrostatic potential fitting using Merz−Singh−Kollman schemes.

correlation energy leads the expected MP2 interaction energy at the basis set limit of −15.12 ± 0.74 kcal mol^{-1}.

Although the parallel corannulene dimer has a large positive SCF interaction energy (10.86 kcal mol^{-1}) at the separation of 3.2 Å calculated with the 6-311G(2d) basis set, it is overcome by the strong attractive dispersion interaction (−24.25 kcal mol^{-1}). Consequently, the dimer has substantially large bonding energy (−13.39 kcal mol^{-1}). Recently, we reported the calculations of benzene dimers and found that the parallel dimer was strongly stabilized by the dispersion interaction.[12,23] The parallel (D_{6h}) benzene dimer was found to have an optimal separation of 3.8 Å. At this separation the calculated interaction energy of the benzene dimer is −3.06 kcal mol^{-1}, including the correlation energy of −7.34 kcal mol^{-1}.[16] The calculated electron correlation energy of the corannulene dimer (−24.25 kcal mol^{-1}) at the optimal separation (3.2 Å) is about 3 times larger than that of the benzene dimer. Clearly, the stronger attractive dispersion interaction is the cause of the shorter optimal separation of the corannulene dimer. If the corannulene dimer is assumed to represent only a part of C60 dimer, the dispersion interaction between C60 dimer would be larger than that of the corannulene dimer, since the dispersion interaction is always attractive and accumulates. This suggests that C60 dimer would have strong attractive dispersion interaction, and this interaction would be the dominant term in the interaction of C60 dimer.

We used the corannulene dimer as a model of the fullerene dimer. Bowl-shaped C20 dimer is another candidate for the model. But the C20 has a lot of dangling bonds. Due to this reason, we hesitated to use the C20 dimer as a model. On the other hand, the terminal hydrogens of corannulene may give slightly negative charge to the C20 framework of corannulene and cause the electrostatic repulsion, which does not exist in the C60 dimer. To evaluate the effect of the terminal hydrogens, the electrostatic interaction was estimated using the atomic charges obtained by electrostatic potential fitting of the MP2/6-311G(2d) wave functions of the corannulene monomer. The calculated atomic charges are shown in Figure 2. The electrostatic interaction between corannulene units was calculated using these atomic charges. The calculated electrostatic interaction at the separation of 3.2 Å is 1.67 kcal mol^{-1}, which is 15% of the repulsive HF interactions energy (10.86 kcal mol^{-1}).

The calculated inter-ring distance of 3.2 Å at the optimal separation is substantially smaller than twice the Pauling's van der Waals radius (1.7 Å)[31] of the carbon atom and is also shorter than the separation of the graphite plane (3.35 Å). Further shorter contact has been observed in condensed-phase C60.[1] The experimentally observed nearest-neighbor distance and sphere diameter of C60 are 10 and 7 Å, respectively, which leads to the separation of 3 Å. The separation of the corannulene dimer is intermediate between those of C60 and graphite. The optimal separation is determined by the balance of repulsion and attractive dispersion interactions. The shorter separation of corannulene dimer suggests that the attractive interaction overcomes the repulsion at the separation of 3.35 Å (separation of graphite). The repulsion interaction between the corannulene molecules should be smaller than the one between the graphite planes of the same number of carbon atoms at the same separation. Due to the bowl shape of the corannulene molecule, the carbon atoms of the central five-membered rings are mainly responsible for the repulsion interaction of the corannulene dimer. The repulsion interactions of the other carbon atoms are less important, since it decreases rapidly by the increase of the interatomic distance. On the other hand, all the carbon atoms have strong repulsion interactions in graphite. Although the dispersion interaction between corannulene molecules should be smaller than that of graphite, the dispersion interaction converges more slowly compared with the repulsion interaction. Consequently, relatively stronger attractive dispersion interaction makes corannulene molecules stay closer than in the case of graphite planes.

We compare the calculated intermolecular interaction potential of corannulene dimer with those calculated from the atom−atom potential parameters[3,4] used for MD simulations of C60.[5,6] We used the parameters reported by Steel[3] and by Gauster.[4] These atom−atom potential parameters were determined based on experimental measurements of graphite. The calculated intermolecular interaction potentials of the corannulene dimer using these parameters have an optimal separation of 3.0 Å, which is shorter than the separation of graphite planes. The depths of the potentials are −19.7 and −24.3 kcal mol^{-1}, respectively. The depth (−13.39 kcal mol^{-1}) of the potential obtained from our MP2/6-311G(2d) level calculation is much shallower than these potentials.

The intermolecular interaction potentials in the repulsive region calculated with these atom−atom potential parameters are steeper than that obtained by our ab initio calculations. These Lennard-Jones (12−6) parameters are determined based on the experimental measurements of the intermolecular distance and heat of sublimation of graphite. However, these data are essential only for the region around the potential minimum. Thus, the shape of the potential around the minimum is determined with some degree of accuracy, while the shape of the potential away from the minimum such as the repulsive region depends to a great extent on the mathematical expression selected to describe the potential. Thus, the disagreement of the potential in the repulsive region between ours and theirs suggests that the mathematical expression of the Lennard-Jones type atom−atom potentials may have the defect to describe the interaction in the repulsive region.

Conclusion

We have found that the parallel (D_{5h}) corannulene dimer is stabilized with strong attractive dispersion interaction. The calculated optimal separation (3.2 Å) between two five-membered rings is considerably shorter than that (3.8 Å) of the parallel (D_{6h}) benzene dimer and that (3.35 Å) of graphite planes. The bowl shape of the corannulene molecule makes the dimer stay that close. The calculated potential is substantially shallower than those calculated with Steel's and Gauster's atom−atom potential parameters based on graphite data, which are commonly used for the MD simulations of C60. The intermolecular interaction potential in the repulsive region from our ab initio calculations is less steep than those obtained from these Lennard-Jones type atom−atom potential parameters, suggesting that these atom−atom potentials may have defects in the description of the repulsive region of C60. Therefore, we believe that intermolecular potential parameters from our ab initio calculations would be more reliable than the parameters previously proposed for C60.

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