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論文要旨 (博士)

学位論文 題目	Computational Study on the Relative Stabilities of Fullerenes and <i>quasi</i> -Fullerenes (フラーレン及び準フラーレンの相対安定性に関する計算化学的研究)
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Computational chemistry has consistently supported fullerene research thus playing a useful role in the studies of carbon clusters. Although fullerenes have been studied for some 15 years, many interesting aspects in this field still remain unexplored both experimentally and theoretically. This thesis provides a survey of the studies on the relative stabilities of isomeric fullerenes  $C_n$  ( $n$  from 20 to 120), in particular of the  $C_{76} - C_{94}$  IPR structures. The smaller systems of  $C_{32}$  and  $C_{36}$  (including some *quasi*-fullerenes) have also been treated particularly because of the recent new experimental developments. The outcomes of combined quantum-chemical and statistical-mechanical calculations are analyzed and compared with experimental data, wherever they are available. Full geometry optimizations are performed and the interisomeric energies obtained are subjected to further advanced checking. This study produces the mole fractions of the fullerene isomers, showing that they exhibit considerable temperature dependencies. The results consequently help in finding experimental conditions that favor particular isomers. The results of our computations have demonstrated that the fullerene isomerism cannot be really understood without considering temperature effects. The temperature effects are however evaluated for the thermodynamic equilibrium, *i.e.*, derived from the standard Gibbs function. The need for the entropy terms comes directly from the fact that fullerenes are synthesized at very high temperatures. In some involved cases (e.g.  $C_{36}$ ,  $C_{72}$ ,  $C_{80}$ , *etc.*), other than ground-state structure in fact dominates in high-temperature mixtures of fullerene isomers in our computations. On molecular level, the temperature effects result from a complex interplay among rotational, vibrational, potential-energy, chirality factors, and can help in elucidation of synthetic conditions for particular isomers. This microscopic representation enables a molecular interpretation of experimental facts. Such temperature effects can never be seen if only energetics is considered, while entropy terms are neglected. Even though it is difficult to estimate a degree to which the presumption of the inter-isomeric equilibrium is satisfied in an experiment, our thermodynamic-equilibrium treatment already produced a reasonable agreement with experiment in eight isomeric fullerene systems ( $C_{76} - C_{94}$ ), without any serious failure. The results in the thesis support the belief in the treatment wider applicability, and thus, encourage our ongoing further investigations for various fullerenes systems (which are experimentally detected or even separated but not yet structurally characterized). Our computational results are obviously useful for both fullerene and materials science.