Ab initio MO Optimizations of Osmiumtetracarbonyldihydride and Metallacyclophanes with two Osmium Atoms and their Molecular Complexes with Different Guests

Inge Warttmann, Günter Häfelinger*

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Z. Naturforsch. **53b,** 1223–1235 (1998); received July 22, 1998

Geometry Optimizations, Osmiumtetracarbonyldihydride, Bis-Osmium-Metallacyclophanes, Host-Guest Complexes, Tetrafluoroethene

Ab initio Hartree-Fock (HF) and density functional (DFT) optimizations on the test molecule osmiumtetracarbonyldihydride (**13**) with various basis sets show that the lanl2mb pseudopotential basis set for osmium leads in the HF approximation to more reliable molecular geometries than the DFT calculations. This HF procedure was used for the optimizations of molecular geometries of three isomeric 4,4,4,4,17,17,17,17-octacarbonyl-4,17-diosma[7.7]*ortho-*, *meta-* and *para*cyclophanes **1** to **3**, of which **3** was found to be predestined for formation of various host-guest complexes with possible guests benzene (**4**), fluorobenzene (**5**), 1,3,5-trifluorobenzene (**6**), 1,2,4,5-tetrafluorobenzene (**7**), hexafluorobenzene (**8**), fluoroanil (**9**), tetrafluoroethene (**10**), tetracyanoethene (**11**) and aniline (**12**). Results of optimized host-guest geometries are presented graphically for inclusions and associations of guest **4** to **12** with **3**. Calculated lanl2mb interaction energies, after correction for basis set superposition error (BSSE), remain favourable only for inclusion of **5** and associations of **5**, **10**, **11** and **12**. Additionally lanl2dz single point calculations for inclusion, which may not need BSSE correction because of the improved basis set, are favourable for **6** and **12**. According to lanl2mb HOMO and LUMO energies, **3** may as well easily donate or accept electrons. This may be an interpretation to the surprising effect, that Mulliken total charges are positive on the electron accepting guest molecules **4** to **11**. There are geometrical peculiarities in the optimized host-guest complexes for inclusion and association. Fluorine atoms of **5** to **10** and nitrogen atoms of a cyano group of **11** and the amino group of **12** like to come close to one or two carbonyl groups. Similar distances of 2.70 Å to 3.57 Å between the O atom of the carbonyl group and the F atom or N atom appear in all optimizations of inclusion and association of **5** to **12** except in the case of association of tetrafluoroethene (**10**).

* Reprint requests to Prof. Dr. G. Häfelinger. E-mail: guenther.haefelinger@uni-tuebingen.de