

EVALUATION OF HELICAL TWISTING POWER OF AN OCTAHEDRAL METAL COMPLEX ON THE BASIS OF A LOCAL STRUCTURE MODEL

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Recently we have interested in the Δ Isomerism of transition metal complexes as a source of chirality in liquid crystals.^{1,2)} It is reported that Δ -[Ru(acac)₂L], in which L and acac denote a mesogenic derivative of 4,4'-bipyridine (or 5,5'-(4-octyphenyloxycarbonyl)-2,2'-bipyridyl), and acetylacetonate ligand, respectively, gives an extremely high helical twisting power when it is doped in *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA). The high value of helical twisting power for these molecules may be related to the presence of the host molecules which interact strongly with a dopant molecule. The large twisting of such host molecules may propagate through a host medium, inducing the sequential twist of other host molecules. In order to examine such a possibility, we performed the theoretical simulation on the microscopic structure in the vicinity of a dopant molecule. It was attempted to elucidate a simple model for helical twisting power on the basis of the attractive interaction between the host and dopant molecules.

In order to evaluate the interaction of a dopant with host molecules, we calculated the configuration of a triad system consisting of two MBBA molecules and Δ -[M(acac)₂L], whose optimized structure is shown in: Figure.1. For simulation, it was assumed that the potential energy of a dopant molecule in a MBBA medium was represented by the intermolecular interaction of a dopant and two host molecules. A dopant molecule was assumed to be Δ -[Mg(acac)₂L] with no d-electron instead of Δ -[Ru(acac)₂L] with 3 d-electrons. This was because the contribution of d-electrons to interaction energy was expected to be negligible. The interaction of ligands (L) of a dopant with MBBA was thought to be a main factor in stabilizing the system. The geometry optimization of the

system was performed at the HF/3-21G** level with the GAUSSIAN03 program. After such an optimization procedure, the energy of the triad system was calculated by varying the twisting angle or the dihedral angle of O-N-O-N of two host molecules. In this procedure, more precise energy was calculated for [Ru(acac)₂L] (not [Mg(acac)₂L]), in which HF/LANL2DZ was used for Ru (II) atom and HF/6-31G** for other atoms. As a result, the dihedral angle of two hosts (O-N-O-N) was calculated to be -32 ° for this dopant. Notably the twisting direction of these two host molecules was coincident with the left-handed helicity as experimentally observed for the cholesteric phase induced by Δ-[Ru(acac)₂L]. It was intended to derive the expression for helical twisting power on the basis of the above local model.

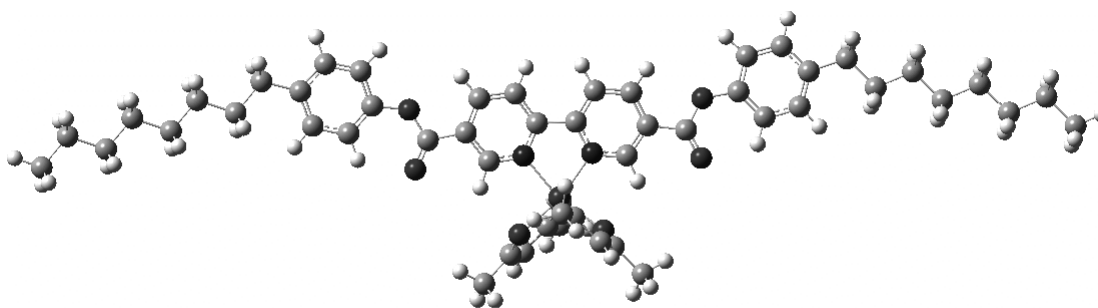


Fig. 1 Optimized structure of dopant

Reference

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