Computational Analysis of Dipole Moment Enhancement in Hydrogen-bonded Molecular Crystal 5-Bromo-9-hydroxyphenalenone

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Hydrogen bonding has been a topic of considerable interest due to its relevance in chemistry, physics and biology. In the field of materials science, the hydrogen-bonded organic and inorganic compounds exhibit various interesting transition phenomena, including (anti-)ferroelectric transitions. The hydrogen bonding is involved in these transitions in forms of proton transfer, isotope effect and enhancement of spontaneous electric polarization [1].

5-Bromo-9-hydroxyphenalenone (BHP, Figure 1), which has O-H…O type intramolecular hydrogen bond, exhibits a paraelectric – antiferroelectric phase transition in the D compound, while the H compound exhibits no phase transition [2]. In this work, we have investigated the effect of the intermolecular interactions on the dielectric properties in BHP. By means of the fragment molecular orbital (FMO) method, Bader’s theory of “Atoms in Molecules” (AIM) and Monte Carlo simulation, we have shown that relative configurations of hydrogen atom strongly affect the induced dipole moment via intermolecular hydrogen bonding. It is also shown that the dipole induction is mainly due to the difference of the electrophilicity between enolic and carbonyl oxygen in BHP molecule [3, 4].

Figure 1. Intermolecular hydrogen bond chains in BHP (Arrows indicate transverse dipole moment).


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