

Quantum delocalization of benzene in the ring puckering coordinates.

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The effect of quantum mechanical delocalization of atomic nuclei on the conformation of the six-membered ring structure in two hydrocarbons, cyclohexane and benzene, is investigated using ab initio path integral approach. A striking feature of benzene species is revealed using ring puckering coordinate representation, which demonstrates that the zero point motion of the heavy atom skeleton dominates over the out-of-plane thermal motions of the ring. Even more unexpected is the fact, that this is true not only at low temperature of 150 K, at which such behavior would not be surprising, but also at room temperature, where the nuclear quantum effects are usually of lesser importance, especially in the case of such heavy nuclei as carbon. In view of this finding the planar conformation of benzene, whose equilibrium ($T = 0$ K) geometry results from the well-known properties of the electronic structure, can be elucidated also at nonzero temperature. According to our simulations, it appears as a consequence of quantum delocalization of the carbon nuclei rather than a trivial time average over the classical configurations of the puckered ring. This interesting behavior is contrasted with the clearly nonplanar structure of cyclohexane, whose ring puckering states can be unequivocally assigned even if the nuclear delocalization is taken into account.

Słowa kluczowe

nuclear quantum effects, quantum delocalization, ring puckering, aromaticity, ab initio path integrals

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