عنوان مقاله:

Theoretical Investigation & NBO Analysis on the conformational equilibria of 3-substituted cyclohexane-1,3,5-triones

محل انتشار:

دومین همایش ملی تکنولوژی های نوین در شیمی و پتروشیمی (سال: 1394)

تعداد صفحات اصل مقاله: 6

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خلاصه مقاله:

The conformational equilibrium of 2,4,6-trimethoxy- (1), 2,4,6-trimethylthio- (2), 2,4,6-trimethylseleno- (3), 2,4,6-trifluoro- (4), 2,4,6-trichloro- (5), 2,4,6-tribromo cyclohexane-1,3,5-trione (6) have been studied by means of ab initio and hybrid density functional theory methods and NBO interpretation. Both methods used showed that the above compounds exist predominantly in the axial chair conformation and the axial conformation stability increased from 1 to its analogous 3 and also from 4 to its analogous 6. The NBO analysis of donor-acceptor (→π*) interactions showed that the GAE (generalized anomeric effect) increases from compound 1 to compound 3 and also from compound 4 to compound 6. However, the variations of the calculated Δ(μeq - μax) values are not in the same trend observed for the corresponding GAE and ΔG values. The axial predominance for 3 and 6 is related to hyperconjugation effects between the σC-X and the π*CO orbitals. This interaction is stronger for 3 and 6 than in the case of 1 and 4, where the GE (gauche effect) in the equatorial conformation should be more effective in conformational stabilization. These findings led to the proposal that the calculated GAE values are more significant for the explanation of the axial conformational preferences of compounds 1-6 than the dipole-dipole repulsion effects. The correlations between the GAE, GE, dipole-dipole interactions, donor and acceptor orbital energies and occupancies, conformational energies, .structural parameters and conformational behavior of compounds (1-6) have been investigated in the vapor-phase

کلمات کلیدی:

DFT, Generalized Anomeric Effects, Conformational Analysis, Substituted Cyclohexanones, Ab initio, NBO