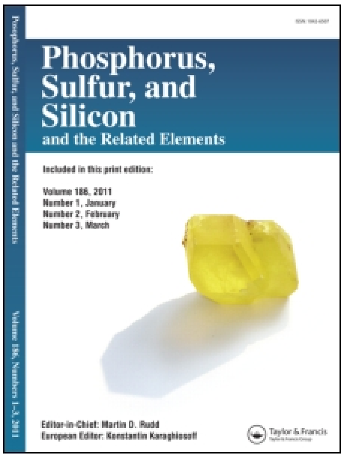

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Comparative Conformational and Electronic Interaction Studies of Some α-Diethoxy-Phosphoryl – Carbonyl Compounds and their α-Ethylsulfonyl Analogues

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The analysis of the IR, ^{13}C NMR data along with the *ab-initio* calculations of some α-diethoxyphosphoryl- and α-ethylsulfonyl-carbonyl compounds indicated that the most stable *gauche* rotamer for both series is stabilized by charge transfer.

Keywords: α-phosphoryl- and α-sulfonyl-carbonyl compounds; conformational studies; electronic interaction

Our previous studies[1-3] on some β-carbonyl sulfides, β-carbonyl sulfoxides and β-carbonyl sulfones indicated that these compounds prefer the gauche conformation. The stability of their gauche conformers has been ascribed to π^*_{CO}/σ_{C-S} and π_{CO}/σ^*_{C-S} orbital interactions.

However, in the case of the β-carbonyl sulfones there is an additional stabilization due to electrostatic and charge transfer interactions between $O_{(CO)} \rightarrow S_{(SO2)}$ and $O_{(SO2)} \rightarrow C_{(CO)}$ atoms, being the latter interaction the stronger one.

It should be pointed out that for closely related molecules the σ_{C-P} and σ^*_{C-P} energy levels are reasonably close to those of the σ_{C-S} and σ^*_{C-S} orbitals. So, it became of interest in the present communication to report the study of the α-diethoxyphosphoryl carbonyl compounds $(EtO)_2P(O)CH_2C(O)X$ (I)(X = Me, ϕ, OEt, NEt_2 and SEt) by IR and ^{13}C NMR spectroscopies and *ab-initio* calculations in order to compare these data with those previously reported[1-3] for the α-ethylsulfonyl carbonyl compounds $EtSO_2CH_2C(O)X$ (II).

The single carbonyl band observed in the IR spectra of compounds (I) along with the good linear correlation between their negative carbonyl frequency shifts (Δν) and the negative carbonyl frequency shifts for the gauche rotamer of series (II), is indicative that the unique rotamer of se-ries (I) has also the gauche geometry.

The absolute values of the carbonyl frequency shifts for series (II) are larger than those of series(I) and both sets follow approximately the electron affinities of the π^*_{CO} orbital of the parent compounds.

Moreover the higher shielding of the carbonyl carbon for series (II) in relation to those of series (I) are in line with the IR data and strongly suggest the occurrence of the $O_{(PO)} \rightarrow \pi^*_{CO}$ charge transfer for series(I) which is weaker than the $O_{(SO2)} \rightarrow \pi^*_{CO}$ interaction for series (II).

The 3-21G* computations for the methyl derivative of series (I) corroborate the above conclusions for the gauche geometry of the α-phosphoryl carbonyl compounds.

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