

Phosphorinane and enol rings in one molecule. Evidence for reciprocal stabilization of half-chair conformations

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Abstract

The X-ray crystal structure of 2-(2',4'-dioxo-3'-pentyl)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (2) reveals significant half-chair distortion of the axially oriented cis-enol ring. The molecule also undergoes in-plane deformations. $R(O...O) = 2.410 \text{ \AA}$ in the enol moiety indicates a very strong hydrogen bonding. The enol content, δ OH and thermodynamic parameters for the axial-equatorial conformational and keto-enol equilibria were obtained from ^1H , ^{31}P NMR and IR measurements in comparison with the planar 4,6-dimethyl isomer (1) containing equatorially oriented enol ring. The X-ray single crystal structure of 5,5-dimethyl-2-(methoxycarbonyl-3'-oxo-2'-butyl)-2-oxo-1,3,2-dioxaphosphorinane (3) reveals the unusual half-chair conformation of the dioxaphosphorinane cycle disposed a trans-enol ring substituent. ^1H , ^{31}P NMR and IR solution data support the same structure displays a strong conformational preference while the minor forms are chair conformers with an axial or equatorial cis-enol ring.

Keywords

β -dicarbonyls, Conformational equilibrium, Hydrogen bonding, Keto-enol equilibrium, Phosphorinane, Tautomer