

Molecular structure of 2-*tert*-butyl-2-oxo-1,3,2-dioxaphosphepine and its benzo derivative

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Abstract

X-ray structure investigation of the title compounds displays a chair form with equatorial alkyl substituent. ¹H NMR and PM3 semiempirical calculations have been also applied and the effect of the planar fragment on the chair–twist-boat equilibrium has been observed.

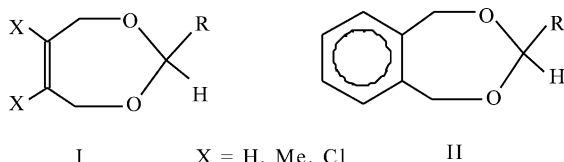
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Keywords: Seven-membered unsaturated phosphonates; X-ray crystallography; ¹H NMR spectroscopy; PM3 calculations

1. Introduction

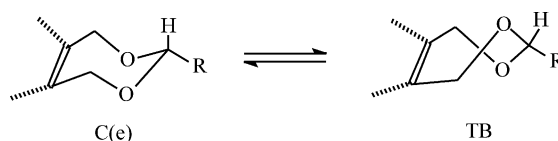
Acetals based on *cis*-2-butene-1,4-diol are recognized to be attractive for the stereochemical investigations, devoted to conformers reactivity [1–4].

According to numerous physical (including direct) methods 2-alkyl (aryl) substituted 1,3-dioxacyclohept-5-enes and their analogues (**I**) and (**II**) exhibit examples of chair(e) and twist-boat conformations[5–13].



Combined IR and NMR data imply that (i) the content of the chair form in equilibrium mixture increases as the steric demand of R group increases. (ii) variation of planar fragments was established to enrich an equilibrium by

a flexible partner in the following series: orthoxylylenic < *cis*-butylenic < dimethyl (dichloro)butylenic.



When S [14], As [15–17], Sb [18–19] or P [20–25] atoms were built-in seven-membered cycles (**I**) and (**II**) instead of C² the influence of the planar fragments was in line with that found for acetals. Structural analysis of the varied 7-membered ring organophosphorus molecules have been actively pursued [26–30] but the steric impact of the exocyclic surrounding at phosphorus atom on the conformational behaviour has not been discussed specially. Compounds (**III**) and (**IV**) that encompass Bu^t groups were prepared to examine their spatial structure by X-ray, IR and ¹H NMR methods including PM3 semiempirical calculations. The presence of a bulky group adjacent to phosphorus atom allowed the chair conformation with axial alkyl substituent to rule out. We anticipated that both (**IV**) and probably (**III**) could adopt a chair conformation in

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