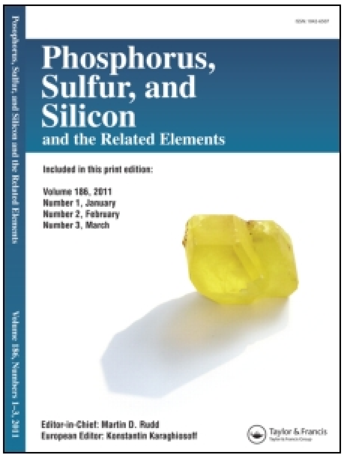

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PHOSPHORINANE AND ENOL RINGS IN ONE MOLECULE. EVIDENCE FOR RECIPROCAL STABILIZATION OF HALF-CHAIR CONFORMATIONS

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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 Å 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 equilibriums were obtained from ^{1}H, ^{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. ^{1}H, ^{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.

Key Words: Conformational equilibrium; β-dicarbonyls; hydrogen bonding; keto-enol equilibrium; phosphorinane; tautomer.

Dicarbonyl compounds have been the subject of numerous studies.[1,2] The introduction of bulky alkyl substituent on the central carbon of the β-dicarbonyls depresses the enol content almost to zero, preventing a detailed analysis of enol form. Even in this case the enol ring was considered as planar, since downfield δ_{OH} shifts were observed in the ^{1}H NMR spectra. The conformational properties of β-dicarbonyl compounds received little attention.

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We have recently described, that the phosphorus-containing bulky substituents are most suitable for producing steric pressure on the β-substituents without decreasing enolization,[3] because of their electron-withdrawing properties. The introduction of the dioxaphosphorinane substituents provided a possibility to vary the direction of the steric pressure.

In the 4,6-dimethyl isomer (**1**) the equatorially oriented enol ring is in the plane of symmetry of the dioxaphosphorinane ring and undergoes only in-plane deformations.[3]

According to the crystal structure, **2** is in its enol form[4]. The P=O bond is perpendicular to the enol ring and equatorial to the chair dioxaphosphorinane ring. The most remarkable features of the enol ring are its deviation from planarity and the tilt of the methyls away from external oxygen atoms, the enol ring adopts a flattened *half-chair* conformation. To our knowledge we have found the first example of a nonplanar enol tautomer.

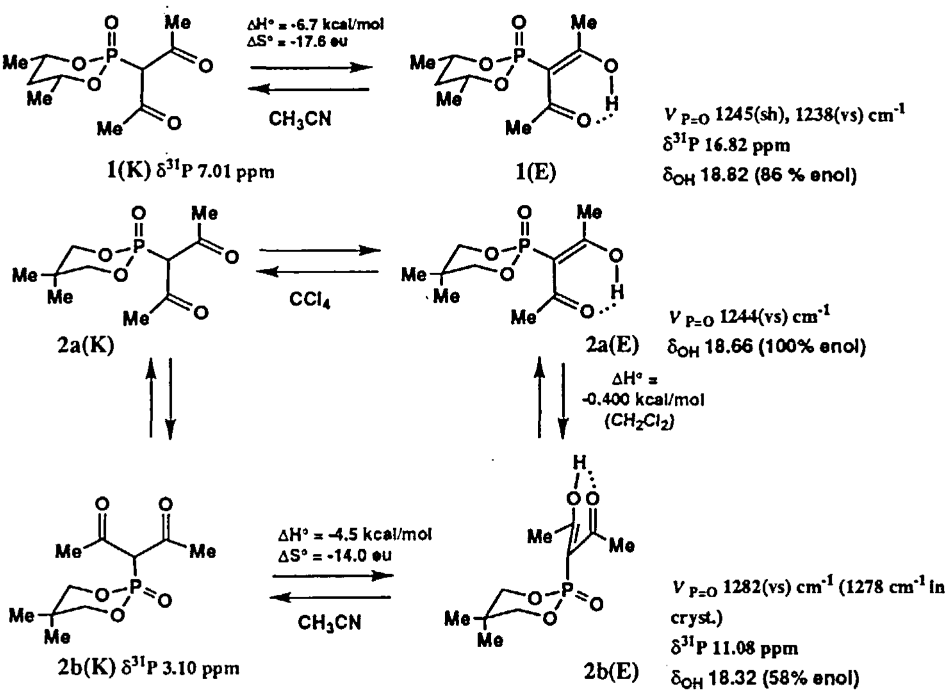
The molecule also undergoes in-plane deformations. The enol inner valence angles are enlarged (2-3°) compared to values for the 3-aryl derivatives of pentane 2,4-dione.[5] R(O...O) = 2.410 Å indicates a very strong hydrogen bonding. Judging from short van der Waals contacts of the enol methyl groups with phosphorinane oxygen atoms, the enol ring deformations and the strengthening of the hydrogen bonding in comparison with pentane-2,4-dione are due to the repulsive intramolecular interactions.

In terms of the two rapidly interconverting chair-ring conformations the less polar equatorial conformer **2a** is predominant in nonpolar solvent (CCl_4), whereas **2b** predominates in CH_3CN, as deduced from IR and ^{31}P NMR data (SCHEME I).[6]

From variable temperature infrared spectra at 476 cm^{-1} **2a** and 488 cm^{-1} **2b** frequencies in CH_2Cl_2 the value of ΔH° was calculated to be -0.440 ± 0.100 kcal/mol (r=0.99) for the interconversion between **2a(E)** and **2b(E)**. Assuming the rotation isomer in **2b(E)** is the same in solution as in the crystalline phase, one would suppose similar distortions as those found by the X-ray diffraction study. In comparison with 2-methyl-2-oxo-1,3,2-dioxaphosphorinane[7] a smaller enthalpic stabilisation of the P=O equatorial conformer was observed and the difference (0.9 kcal/mol) could mainly be attributed to the energetically unfavourable nonplanar effects in the axially oriented enol ring.

^1H NMR experiments register the upfield shift of the δ_{OH} (0.50 ppm) from **1(E)** to **2b(E)** in CH_3CN (0.16 ppm in CCl_4) in which the dramatic difference in the conformational composition of these compounds have been found by IR. This indicates a relative weakening of the hydrogen bonding in **2b(E)**, compared with **2a(E)**.

The enol content of **2** is less than that in of **1**, which would be consistent with relative destability of the enol form in **2b** caused by the nonplanar effect. A smaller



1(K) $\delta^{31}P$ 7.01 ppm

1(E)

$\nu_{P=O}$ 1245(sh), 1238(vs) cm^{-1}
$\delta^{31}P$ 16.82 ppm
δ_{OH} 18.82 (86 % enol)

2a(K)

2a(E)

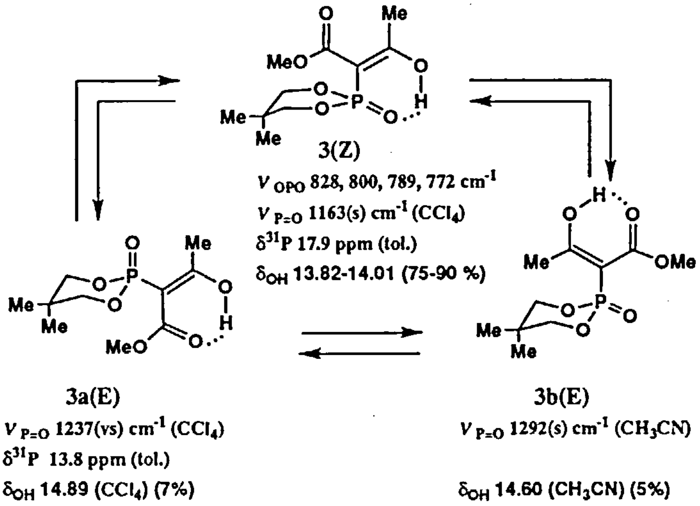
$\nu_{P=O}$ 1244(vs) cm^{-1}
δ_{OH} 18.66 (100% enol)

2b(K) $\delta^{31}P$ 3.10 ppm

2b(E)

$\nu_{P=O}$ 1282(vs) cm^{-1} (1278 cm^{-1} in cryst.)
$\delta^{31}P$ 11.08 ppm
δ_{OH} 18.32 (58% enol)

SCHEME I



3(Z)

ν_{OPO} 828, 800, 789, 772 cm^{-1}
$\nu_{P=O}$ 1163(s) cm^{-1} (CCl_4)
$\delta^{31}P$ 17.9 ppm (tol.)
δ_{OH} 13.82-14.01 (75-90 %)

3a(E)

$\nu_{P=O}$ 1237(vs) cm^{-1} (CCl_4)
$\delta^{31}P$ 13.8 ppm (tol.)
δ_{OH} 14.89 (CCl_4) (7%)

3b(E)

$\nu_{P=O}$ 1292(s) cm^{-1} (CH_3CN)

δ_{OH} 14.60 (CH_3CN) (5%)

SCHEME II

enthalpy of enolization of the nonplanar enol **2b** in comparison with the planar **1** is observed (by 2.2 kcal/mol). As the intramolecular hydrogen bond of β-dicarbonyl compounds is the main reason for the stabilisation of the enol tautomers[1,2], a relative weakening of the hydrogen bonding because of deformation of the enol conjugated system is obvious and leads to this energy difference.

It was also of interest to reveal reverse influence of the enol conformation on the conformation of a substituent. It was known, that half-chair conformation is relatively rare for the phosphorinane ring, being obviously of very high energy.[8] We have synthesized β-keto-ester **3** and found that it is a mixture of trans and cis-enol forms.[9] The X-ray single crystal analysis shows that **3** exists in the trans-enol tautomeric form **3(Z)** (R(O...O) = 2.506 Å) and the conformation of the dioxaphosphorinane ring was *half-chair.* This is a first example of half-chair conformation of a phosphorinane cycle featuring hydrogen bond. NMR and IR solution data support the same structure displays a strong conformational preference while the minor forms are chair conformers with an axial and equatorial cis-enol ring (SCHEME II).

The deformation of the enol ring and the flattening of the phosphorinane ring are a result of severe steric hindrances in these molecules and can be conformationally dependent.

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