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Notes

Phosphorus-Stabilized Nonplanar Enol Tautomer of Pentane-2,4-dione

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The planarity of a β-dicarbonyl end ring provides the optimum geometry for significant hydrogen-bond strengthening by delocalization of the π-conjugated system.[2] This concept is based upon a growing number of structure determinations of uncrowded enols.[2a–d,3] The introduction of a bulky alkyl substituent[4] on the central carbon of a β-dicarbonyl depresses the enol content almost to zero.[5] Even so, the enol ring is considered to be planar,[2a,6] since downfield δ_{OH} shifts are observed in the ^{1}H NMR spectra.

We have recently reported that phosphorus-containing bulky substituents are most suitable for producing steric pressure on their β-substituents without decreasing enolization[7] because of their electron-withdrawing properties. The introduction of dioxaphosphorinane substituents provided the opportunity 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.[7]

We report here on the X-ray structure of conformationally mobile[8] 2-(2′,4′-dioxo-3′-pentenyl)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (2), which *reveals that the axially oriented enol ring in 2 is deformed from planarity.*

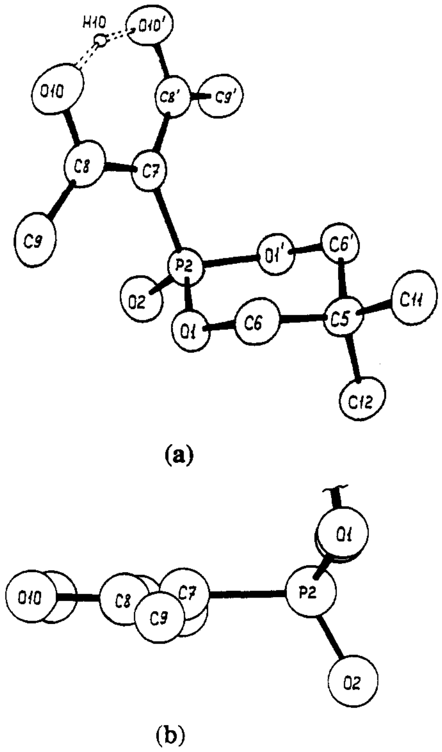
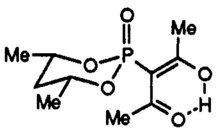
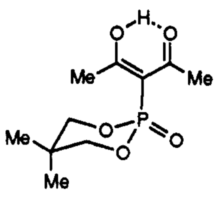


Figure 1. (a) OPTEP drawing of molecule 2. (b) "Side on" views, showing half-chair conformation of deformed enol ring (the phosphorinane cycle is omitted for clarity).



1



2

The known compound 2[7] was prepared by the carbenoidP–H insertion method[9] and crystallized from ether–chloroform. An X-ray structural analysis of 2 was undertaken to investigate the lateral steric pressure on the methyl groups of the axially oriented enol ring that might be expected for a substituent in this position.[10] A list of selected bond lengths, valence, torsion and interplanar angles, and intramolecular short contacts between nonbonded atoms for the molecule 2 is given in Table 1. According to the crystal structure, 2 is in its enol form (Figure 1). The crystals of 2 were found to possess a plane of symmetry, reducing the number of parameters (the molecule is specially positioned with a crystallographic

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(1) Current adress: Laboratorie de Chimie de Coordination, 205, Route de Narbonne, 31077 Toulouse Cedex, France.

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(8) A difference in the conformational composition of 1 and 2 was suggested from alterations of the δ_{OH} and the enol content.[7]

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Table 1. Selected Bond Lengths (Å), Valence, Torsion and Interplanar Angles (deg), and Intramolecular Short Contacts (Å) for 2

P(2)–O(1)	1.575(3)	P(2)–O(2)	1.459(3)	P(2)–C(7)	1.787(5)
C(7)–C(8)	1.423(5)	C(8)–O(10)	1.283(5)	O(10)–H(10)	1.237(15)
O(1)–P(2)–O(1′)	104.3(2)	O(1)–P(2)–O(2)	111.7(2)	C(7)–C(8)–O(10)	120.9(4)
C(7)–C(8)–C(9)	124.1(4)	C(8)–C(7)–C(8′)	116.8(5)	O(10)–H(10)–O(10)	154(15)
O(2)–P(2)–C(7)–C(8)	−86.6	P(2)–C(7)–C(8)–O(10)	−176.7	P(2)–C(7)–C(8)–C(9)	6.9
C(8′)–C(7)–C(8)–O(10)	9.9	H(10)–O(10)–C(8)–C(7)	−4.6	C(8)–O(10)–H(10)–O(10′)	−2.4
C(7),C(8),O(10),H(10)[a]/C(7),C(8′),O(10),H(10)				5.0	
C(8),O(10),O(10′),C(8′)/C(8),C(7),C(8)				8.3	
C(8),O(10),O(10′),C(8′)[b]/O(10),H(10),O(10′)				2.4	
C(9), O(1)	2.946	H(9,1), O(1)	2.478	H(9,3), O(1)	2.572
H(9,3), O(2)	2.615				

[a] Deviations (Å): P(2), −0.044; C(9), 0.183. [b] Deviations (Å): P(2), −0.198; C(9), 0.201; C(7), −0.107.

symmetry m).[11] The P=O bond is equatorial to the chair dioxaphosphorinane ring, which is as expected (Table 1).[7,10] The plane of the enol ring is perpendicular to the P=O bond. The remarkable features of the enol ring are its deviation from planarity and the tilt of the methyls away from the O(1),O(1) atoms. As is evident from the interplanar angles listed in Table 1, the enol ring adopts a flattened half-chair conformation.[12] The deviation of the dihedral angles from the planar standard (0° and 180°), as well as the values of the interplanar angles, are a convenient indication of the extent of the distortion. The deviation is close to deviations observed in aromatic structures.[4] To our knowledge, we have found the first example of a nonplanar enol tautomer.

The molecule also undergoes in-plane deformations. The opening of the C(7)–C(8)–C(9) and C(7)–C(8′)–C(9′) angles, a good in-plane deformation test,[7] is smaller (1–2°) than that for 1[7] but enlarged (2–3°) compared to values for the 3-aryl derivatives of pentane-2,4-dione.[3b] R(O···O) = 2.410 Å indicates very strong hydrogen bonding,[2a–d] through this is hardly longer (0.013 Å) than the extremely short value found for isomer 1.[7]

Judging from the short van der Waals contacts of the methyl groups with O(1),O(1′), the enol ring deformations and the strength of the hydrogen bonding (relative to that of pentane-2,4-dione)[3a] are due to repulsive intramolecular interactions.

In conclusion, our results present the first example of a nonplanar β-dicarbonyl enol ring. The various modes of the enol ring deformations can be conformationally dependent.

Experimental Section

X-ray Crystal Structure Analysis of 2. Single crystals of $C_{10}H_{17}O_5P$ were grown from an ether–$CHCl_3$ solution of the compound 2.[7] The crystal were orthorombic, space group $Cmc2_1$ with $a = 8.864(2)$ Å, $b = 8.436(3)$ Å, $c = 16.326(6)$ Å, and $D_{calcd} = 1.35$ g cm^{-3} for $Z = 4$. The intensity data were measured on a CAD4 Enraf-Nonius diffractometer using graphite-monochromated Mo Kα radiation. The size of the crystal used for collection was approximately 0.15 × 0.25 × 0.30 mm^3. A total of 1197 independent reflections were measured of which 703 were considered to be observed [$I \geq 3\sigma(I)$]. The structure was solved by direct methods using the MULTAN[13] program and refined by full-matrix least-squares calculations. Hydrogen atoms were located from a subsequent difference map and refined isotropically in the final cycle. The refinement converged at $R = 0.034$, $R_w = 0.045$. Structure determination and refinement were performed with the SDP program on a PDP 11/23 computer.

The authors have deposited atomic coordinates for this structure at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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[11] The only other case of m crystallographic symmetry of enol reported refers to the crystal structure of bis(m-bromobenzoyl)methane (Williams, D. E.; Dumke, W. L.; Rundle, R. E. *Acta Crystallogr.* **1962**, *15*, 627).

[12] (a) The deformation parameters for the part of the enol ring containing hydrogen bonding are within experimental error. (b) A hydrogen bonding proton of pentane-2,4-dione presented in the drug complex solvate lies 0.36 Å out of the plane.[3a] This distortion probably arises from lattice forces.[2a,3b]

[13] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.