Tetrahedron Letters No. 46, pp 4067 - 4068, 1974. Pergamon Press. Printed in Great Britain.

TETRAETHYL 3,7-DIOXOBICYCLO[3.3.0] OCTANE-2,4,6,8-TETRACARBOXYLATE,

A UNIQUE CASE OF KETOENOL TAUTOMERISM

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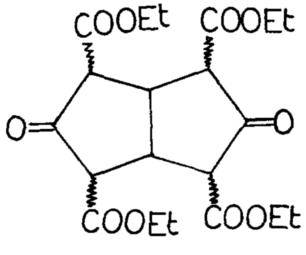
(Received in UK 30 September 1974; accepted for publication 10 October 1974)

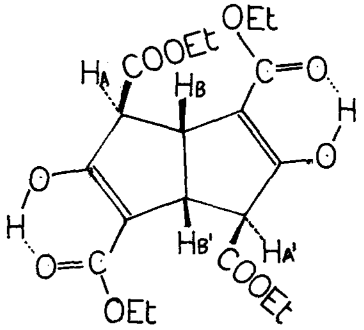
In carbon tetrachloride or chloroform solution, the title compound (I) is 100% enolized at both keto groups. This behaviour strongly contrasts with that of reasonable model compounds, such as ethyl 2-oxocyclopentanecarboxylate and diethyl 2-oxocyclopentane-1,3-dicarboxylate, which show less than 10% enol form in the same solvents. Furthermore, I exists as only one of the many possible bis-enol tautomers, as shown by its nmr spectrum.

In deuteriochloroform the nmr spectrum of I, m.p. 105-7º (ethanol), obtained following published procedures[1,2,3)] shows a broad absorption at δ 10.35 due to both enol protons, and two slightly distorted triplets ($J = 2.7$ Hz) at 3.60 and 3.87, corresponding to the four carbocyclic protons of the bis-enol form. In carbon tetrachloride, these two triplets appear almost undistorted, with the same coupling constant.

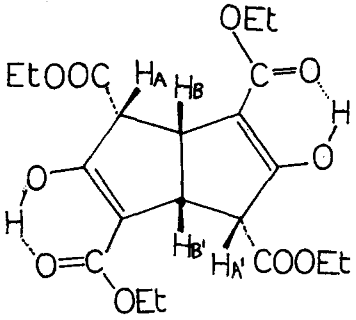
The simplicity of the spectrum points to a highly symmetrical structure, with two enols and only two types of carbocyclic protons. By accepting a <u>cis</u> junction between the two rings, these conditions are only met by structures (II) and (III), both having a C_2 axis of symmetry.



(I)



(II)



(III)

In both structures an AA'BB' system is to be expected for the carbocyclic protons; the simplicity of the spectrum arises from the fact that $J_{AB} \sim J_{AB'} \sim 2.7$ Hz. In structure III, the dihedral angle $H_A - H_B$ is ca. 0°, and according to the Karplus relationship J_{AB} should be higher than the observed value, 2.7 Hz. Therefore structure II is a better choice; the dihedral angle ca. 120° would be in accord with the experimental value for J_{AB}. On the other hand, the observed value for $J_{AB'}$ (2.7 Hz) is similar to other reported homoallylic couplings$^{4)}$.

The rather unusual preference of I for the bis-enol structure II, must have its origin in steric interactions between the ethoxycarbonyl substituents in positions 2-8 and 4-6. This confirms once more the importance of minimizing steric interactions in ketoenol tautomerism$^{5)}$.

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