β-Diketone Interactions. Part 6.[1] X-Ray Molecular Structure of 3-(4-Methoxyphenyl)pentane-2,4-dione, a β-Diketone Enol Tautomer with a Very Strong Hydrogen Bond

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The title compound, $C_{12}H_{14}O_3$, exists only as the enol tautomer in $CDCl_3$ solution and in the solid state. Its X-ray crystal structure reveals a near symmetrical enol ring in which the R(O $\cdots$ O) = 2.449 Å indicates a very strong hydrogen bond. I.r. and n.m.r. [$\Delta\delta(H,D)$] data support this result.

Short internuclear distances between the heavy atoms of a hydrogen bond are normally found when one of the species carries a formal charge.[2] Among OHO hydrogen bonds the shortest R(O $\cdots$ O) are found between such combinations as $H_2O + H_3O^+$ [2.431 Å],[3] $HNO_3 + NO_3^-$ [2.461 Å],[4] and $H_2PO_4^- + H_2PO_4^-$ [2.451 Å],[5] and especially with the many examples of the biscarboxylates, $RCO_2H + RCO_2^-$ [2.40—2.45 Å].[6] It is relatively rare to find neutral systems with very strong hydrogen bonds, although some, such as ureaphosphoric acid, are known with R(O $\cdots$ O) = 2.43 Å.[7] Recently a neutron diffraction study of the complex [Co_2{$H_2N(CH_2)_2OH$}$_3$]$^{3+}$ has shown the presence of OHO hydrogen bonds as short as 2.390 Å, but again between oxygens of which one is formally charged.[8]

The intramolecular bonding of the enol tautomers of β-diketones (1) is generally considered to be strong, but not very strong.[9] This is exemplified by pentane-2,4-dione (PD) itself, for which R(O $\cdots$ O) = 2.535 Å was recently recorded for this molecule in the drug complex solvate, diphenylhydantoin-9-ethyladenine–pentane-2,4-dione.[10] A derivative of pentane-2,4-dione which is crystalline is 3,3'-trithiobis(pentane-2,4-dione), and this molecule shows a shorter hydrogen bond [2.461 Å].[11]

(1)
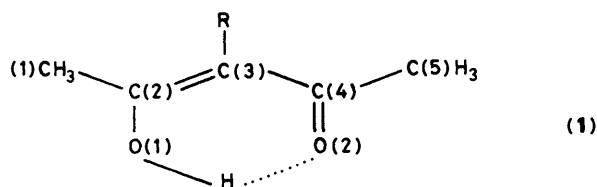
It was once suggested that the hydrogen bond of pentane-2,4-dione could be strengthened by substitution at the 3-position.[12] Apart from the trithio derivative mentioned above, which does show a shorter hydrogen bond, this theory has remained untested presumably because of the lack of suitably crystalline derivatives that carry substituents at the 3-position. We have now prepared a new compound, 3-(4-methoxyphenyl)pentane-2,4-dione, which is crystalline and whose i.r. and ^1H n.m.r. spectra indicated it to be entirely of the enol tautomer.

Experimental

Instruments.—I.r. spectra were recorded on a PE 983G spectrometer and n.m.r. on a Bruker WM250 spectrometer (^1H at 250 MHz, ^2H at 38.4 MHz) crystal structure was determined on an Enraf-Nonius CAD-4 diffractometer.

3-(4-Methoxyphenyl)pentane-2,4-dione ($C_{12}H_{14}O_3$).—Lead tetra-acetate was converted into triacetato(4-methoxyphenyl)-lead by the method of Kozyrod and Pinhey.[13] A solution of

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $C_{12}H_{14}O_3$

	x	y	z
O(1)	6 492(1)	5 225(3)	−4 361(1)
O(2)	5 601(2)	7 560(2)	−4 854(1)
O(3)	1 357(1)	5 028(2)	−2 667(1)
C(1)	5 728(3)	3 589(3)	−3 630(2)
C(2)	5 685(2)	5 004(3)	−4 054(1)
C(3)	4 807(2)	6 039(3)	−4 114(1)
C(4)	4 802(2)	7 309(3)	−4 529(1)
C(5)	3 907(2)	8 461(4)	−4 633(2)
C(6)	3 896(2)	5 776(3)	−3 730(1)
C(7)	3 026(2)	4 816(3)	−3 932(1)
C(8)	2 209(2)	4 580(3)	−3 565(1)
C(9)	2 220(2)	5 313(3)	−2 988(1)
C(10)	3 071(2)	6 265(3)	−2 778(1)
C(11)	3 888(2)	6 486(3)	−3 148(1)
C(12)	1 329(3)	5 799(4)	−2 075(1)

triacetate(4-methoxyphenyl)lead (2.22 g, 4.5 mmol) and pyridine (2 cm³, 13.5 mmol) in $CHCl_3$ (7 cm³) was added dropwise to a solution of PD (20.5 cm³, 205 mmol) in $CHCl_3$ (7 cm³). The mixture was stirred for 24 h at 40 °C, diluted with $CHCl_3$ (20 cm³) and twice extracted with water (2 × 20 cm³) and twice with 3M H_2SO_4 (2 × 20 cm³). The washings were back extracted with $CHCl_3$ (4 × 10 cm³). The combined $CHCl_3$ solutions were dried ($MgSO_4$), and stripped of solvent to yield an orange oil which was purified *via* a silica column with 2% ethyl acetate in 40—60 °C light petroleum as eluant to yield colourless crystals of 3-(4-methoxyphenyl)pentane-2,4-dione (0.15 g, 0.72 mmol, 16% yield), m.p. 62—64 °C (Found: C, 69.4; H, 6.9%. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%); $v_{max.}$ 3 012m, 2 960m, 2 837m (Me), 1 606vs (CO), 1 511vs, 1 442vs, 1 402vs, 1 331vs, 1 283vs, 1 244vs, 1 184vs (the region 1 800—1 100 was overlaid by an intense continuum) 1 100s, 1 031s, 992s, 915m, 832vs, 817m, 794m, 600m, and 596m cm⁻¹; δ_H 1.89 (s, 6 H, Me-PD) 3.84 (s, 3 H, MeO), 6.92 (m, 2 H, CH), 7.10 (m, 2 H, CH), and 16.65 (s, 1 H, OHO).

Crystal Data.—$C_{12}H_{14}O_3$, M = 206.24, monoclinic, a = 12.632(1), b = 8.424(1), c = 21.398(2) Å, β = 96.028(7)°, U = 2 264.2(4) Å³, space group $C2/c$ (No. 15), Z = 8, D_c = 1.210 g cm⁻³, $F(000)$ = 880, λ = 1.5418 Å, μ(Cu-K_a) = 6.7 cm⁻¹, crystal dimensions 0.70 × 0.50 × 0.13 mm.

The structure was solved by direct methods and refined by full-matrix least squares, using absorption corrected data,[14] [Cu-K_a radiation, Ni-filtered, 3° ≤ θ ≤ 70°, h(−15→15), k(0→10), l(0→26), 2 359 reflections, 1 322 independent, $I \geqslant 3\sigma(I)$]. All non-hydrogen atoms were refined aniso-tropically. Methyl and methoxyphenyl hydrogen atoms were
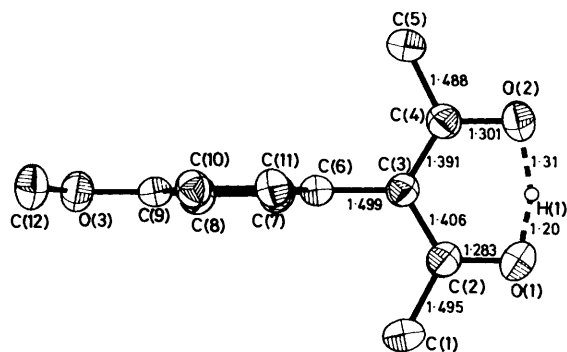
Figure. Molecular structure of 3-(4-methoxyphenyl)pentane-2,4-dione

Table 2. Bond lengths (Å) for $C_{12}H_{14}O_3$

C(2)–O(1)	1.283(4)	C(4)–O(2)	1.301(4)
C(9)–O(3)	1.370(4)	C(12)–O(3)	1.426(4)
C(2)–C(1)	1.495(4)	C(3)–C(2)	1.406(4)
C(4)–C(3)	1.391(4)	C(6)–C(3)	1.499(4)
C(5)–C(4)	1.488(4)	C(7)–C(6)	1.396(4)
C(11)–C(6)	1.382(4)	C(8)–C(7)	1.376(4)
C(9)–C(8)	1.379(4)	C(10)–C(9)	1.377(4)
C(11)–C(10)	1.377(4)	H(1)–O(1)	1.200(39)
H(1)–O(2)	1.312(40)		

Bond angles (deg.)

|			
C(12)–O(3)–C(9)	117.5(3)	O(2)–H(1)–O(1)	154.4(31)
C(1)–C(2)–O(1)	116.5(3)	C(3)–C(2)–O(1)	121.6(3)
C(3)–C(2)–C(1)	121.9(3)	C(4)–C(3)–C(2)	119.1(3)
C(6)–C(3)–C(2)	120.1(3)	C(6)–C(3)–C(4)	120.8(3)
C(3)–C(4)–O(2)	120.9(3)	C(5)–C(4)–O(2)	115.7(3)
C(5)–C(4)–C(3)	123.4(3)	C(7)–C(6)–C(3)	122.7(3)
C(11)–C(6)–C(3)	120.6(3)	C(11)–C(6)–C(7)	116.8(3)
C(8)–C(7)–C(6)	121.3(3)	C(9)–C(8)–C(7)	120.6(3)
C(8)–C(9)–O(3)	115.9(3)	C(10)–C(9)–O(3)	125.0(3)
C(10)–C(9)–C(8)	119.1(3)	C(11)–C(10)–C(9)	119.8(3)
C(10)–C(11)–C(6)	122.4(3)	C(2)–O(1)–H(1)	100.8(17)
C(4)–O(2)–H(1)	100.0(15)		

placed into calculated positions (C–H 0.96 Å, U = 0.10 Å^2), but the enolic hydrogen atom was allowed unrestricted isotropic refinement. A total of 150 parameters were refined. The final residuals R and R_w were 0.043 and 0.056 respectively. All calculations were performed with the SHELX-76[15] and SHELX-86[16] packages of crystallographic programs.

Atom co-ordinates are given in Table 1 and bond lengths and angles in Table 2. The structure and atom labelling are shown in the Figure. Non-hydrogen atom anisotropic temperature factors, hydrogen fractional atomic co-ordinates and isotropic temperature factors, and selected non-bonded distances are available on request from the Cambridge Crystallographic Data Centre.*

Discussion

Although the hydrogen bond in $C_{12}H_{14}O_3$ is short an even shorter one has been found in one of the enol moieties of usnic acid,[17] which has structure (2) with R(O $\cdots$ O) = 2.40 Å. However at 2.449 Å it is definitely in the class of very strong hydrogen bonds and it is the shortest hydrogen bond of a β-

diketone derivative in which the enol is not part of a cyclic system as in (2). And whereas in structure (2) the enol is asymmetric, in $C_{10}H_{14}O_3$ the framework of the enol ring is remarkably symmetric: R[C(2)–O(1)] = 1.283(4) and R[C(4)–O(2)] = 1.301(4) Å; R[C(2)–C(3)] = 1.406(4) and R[C(3)–C(4)] = 1.391(4) Å.

(2)
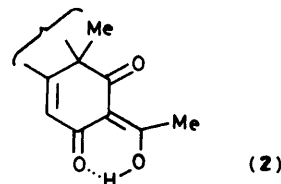
In the molecular structure of PD and the trithio derivative of PD, it is possible to distinguish the double and single C–O and C–C bonds around the enol ring. Thus PD R[C(2)–O(1)] = 1.331(4) whereas R[C(4)–O(2)] = 1.238(4) Å, and R[C(2)–C(3)] = 1.412(4) whereas R[C(3)–C(4)] = 1.338(4) Å.[10] The corresponding bonds in the trithio derivative are 1.325(4) (C–O), 1.267(4) (C=O), 1.444(4) (C–C) and 1.360(4) Å (C=C).[11]

Isaacson and Morokuma predicted[18] that a neutral hydrogen bond would be greatly strengthened if the system with a relatively short R(O $\cdots$ O) were coupled to one with a high degree of delocalization. It was in the hope of generating such a compound that $C_{12}H_{14}O_3$ was synthesized and investigated. The result has been the production of a significantly shorter hydrogen bond than in the parent PD and one that can be classed as very strong. However this strengthening is not due to delocalization since there is no interaction between the phenyl and enol rings, as shown by their almost perpendicular orientations (the dihedral angle between them is 88.9°) and the length of the interconnecting C(3)–C(6) bond [1.499(4) Å]. Steric factors clearly override other molecular energies and it may be repulsion between the phenyl ring and the C(1) and C(5) methyl groups which is responsible for the shortening of the hydrogen bond.

That the hydrogen bond is of the very strong variety can be seen from other evidence. The downfield chemical shift of 16.65 p.p.m. of the enol proton shows it to be more deshielded than that of PD (15.40)[19] but not as deshielded as some other β-diketones such as 3-cyanopentane-2,4-dione (16.90),[20] 3-s-butyl-pentane-2,4-dione (17.5),[21] and even 3-phenylpentane-2,4-dione (16.8).[22] Nevertheless this apparent anomaly is caused by the hydrogen bond of $C_{12}H_{14}O_3$ being *stronger* than any of these and indicates that it is akin to a case 4 hydrogen bond.[9]

In case 4 hydrogen bonding both the proton and the deuterium atom in the corresponding ODO hydrogen bond, are above the potential energy barrier; Δδ(H,D) is negative and less than the difference in chemical shifts of a case 3 hydrogen bond, in which H is above the barrier but D is constrained to its potential energy well. In case 3 instances Δδ(H,D) is positive and *ca.* 0.60 p.p.m. as it is for PD itself.[23] In $C_{12}H_{14}O_3$, Δδ(H,D) is +0.307 which shows that although the D is still confined to one well it is near the top of the energy barrier which has been lowered by the closer proximity of the two oxygens.

The i.r. spectrum of $C_{12}H_{14}O_3$ supports the claim that the hydrogen bond is very strong. There is no v(OHO) absorbance above 1 500 cm^{-1}. Instead there is an extremely broad and intense band underlying the spectral region 1 800—1 100 cm^{-1} and centred at *ca.* 1 400 cm^{-1}. This is characteristic of such bonding.[2] In the spectrum of PD, v(OHO) is centred at 2 750 cm^{-1}.[24]

Clearly the hydrogen bonding of $C_{12}H_{14}O_3$ is unique among the pentane-2,4-dione derivatives so far investigated. This would also explain why this compound exists only as the enol

form, even in $CDCl_3$ solution, whereas in this medium PD exhibits 17% keto tautomer[25] and 3-methylpentane-2,4-dione has 64% keto tautomer.[26]

Acknowledgements

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