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β-DIKETONE INTERACTIONS
Part 12. The structure and properties of 3-(3′,4′,5′-trimethylphenyl)-pentane-2,4-dione, $C_{14}H_{18}O_2$; the hydrogen-bond energy of the enol tautomers of β-diketones*

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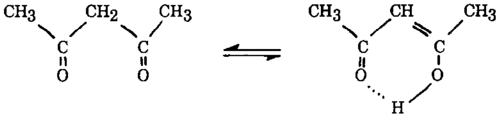
ABSTRACT

The X-ray crystal structure of 3-(3′,4′,5′-trimethylphenyl)pentane-2,4-dione shows it to be the enol tautomer, with a hydrogen bond length $R_{O\cdots O}$ of 2.460 Å, and the enol ring remarkably symmetrical indicating a strong hydrogen bond. The hydrogen-bond energy is estimated to be 110 ± 10 kJ mol^{-1}, a value derived from the infra-red spectrum. In $CDCl_3$ solution 8% of the keto tautomer is present.

INTRODUCTION

The keto/enol equilibrium (**Ik/Ie**) of pentane-2,4-dione lies well to the right-hand side in almost all solvents, and this high concentration of enol is seen as evidence of strong hydrogen bonding which is promoted by the close proximity of the hydrogen donor enol group and the hydrogen acceptor carbonyl oxygen atom. The concentration of enol is sensitive to a variety of external factors such as solvent polarity and temperature, and internal factors such as α and β substituents [2]. Whereas the external influences are thought to be relatively simple, the internal ones are more complex. Thus in CCl_4 as the solvent pentane-2,4-dione is 95% enol, but the 3-methyl derivative is only 48% and the 3-



Ik **Ie**

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ethyl is 47% [3]; 3-cyano and 3-thiomethoxy derivatives are 100% enol [4,5]. We have investigated a number of 3-(4′-substituted-phenyl)-pentane-2,4-diones and these appear also to be 100% enol [6,7], with the exception of the diphenyl which was 98.5% [8].

In previous work on 3-phenylpentane-2,4-diones [6,8] we studied the electronic factors which different *para* substituents might have on the enol ring and the hydrogen bonding; the conclusion was that these have little effect on the latter. This is perhaps understandable since they are well removed from the hydrogen bond. In those compounds studied by X-ray diffraction, the hydrogen bond is short (<2.45 Å) and is significantly shorter than that of pentane-2,4-dione itself (2.535 Å) [9]. Phenyl derivatives were chosen for this study because they give crystalline products suitable for X-ray investigation.

We have now turned our attention to steric effects. If the derivatives with phenyl substituents at the 3-position all have short hydrogen bonds it could be due to steric repulsion between the phenyl ring and the β-methyl group which, in turn, exerts pressure on bond angles at the β-carbon atoms. The molecule could relieve this steric stress by moving the two oxygens closer together. If this were to be the case then further "fine-tuning" of the steric pressure at the phenyl end of the molecule could lead to even closer approach of the oxygen atoms. To test this theory we tried to produce crystals with methyl substituents attached to the benzene ring. Compounds with methyl groups in the 2,6-positions were impossible to produce in suitable crystalline form. However we have been able to make the 3,4,5-trimethylphenyl derivative and we report its structure here.

EXPERIMENTAL

The infra-red (IR) spectrum was recorded on a PE 983-G spectrometer as KBr discs; NMR spectra (^{13}C at 90 MHz; ^{1}H at 360 MHz) were recorded on a Bruker WM360 instrument using $CDCl_3$ solutions.

3-(3′4′5′-Trimethylphenyl)pentane-2,4-dione ($C_{14}H_{18}O_2$)

Lead tetraacetate (9 g, 22 mmol) and trichloroacetic acid were dissolved in $CHCl_3$ (50 cm^3) and 1,2,3-trimethylbenzene (20 cm^3) added dropwise. The mixture was stirred for 30 min after which it was filtered through Celite, washed with water (100 cm^3) and evaporated to one-third of its original volume. Hexane was added to precipitate the solid oligomer which was filtered and dissolved in $CHCl_3$ (50 cm^3). Acetic acid (50 cm^3) was added and the mixture stirred for 1 h before being washed with water (100 cm^3), stripped of solvent and hexane added to precipitate 3,4,5-trimethylphenyllead triacetate as a white solid.

The triacetate (2.1 g, 4.2 mmol) and pyridine (1.5 cm^3) were dissolved in

$CHCl_3$ (25 cm^3) and pentane-2,4-dione (0.45 g, 4.5 mmol) added dropwise. The mixture was stirred at 40°C for 24 h. The resultant mixture was washed with water (20 cm^3) and then 3M H_2SO_4 (2×20 cm^3). The aqueous and acid phases were extracted separately in $CHCl_3$ (10 cm^3). The combined extracts were washed with water (2×25 cm^3), dried over $MgSO_4$, and stripped of solvent. The resultant colourless solid was crystallised from methanol to give yellow crystals of 3-(3′,4′,5′-trimethylphenyl)pentane-2,4-dione (0.57 g, 2.6 mmol, 63% yield), m.p. 99–101°C. Found: C, 75.14; H, 8.23%. $C_{14}H_{18}O_2$ requires: C, 77.03; H, 8.31%.

IR spectrum ν_{max}: 3222m, 3022m, 2982m, 2867m, 2336w, 1751w, 1601vsbr, 1569vs, 1481vs, 1455vs, 1409vs, 1375s, 1339vs, 1255m, 1160w, 1077w, 991vsbr, 921m, 870m, 852s, 817w, 720m, 696w, 670w, 620m, 605w, 526m, 448m, 422w, 409w cm^{-1}. The region 1700–1200 cm^{-1} is overlaid with an intense continuum centred at ca. 1450 cm^{-1}. There is also a broad peak centred at ca. 1000 cm^{-1}.

NMR spectrum $\delta(^1H)$: 1895 (s, 6H, MePD), 2.19 (s, 3H, 3′-Me), 2.29 (s, 6H, 2′,4′-Me), 3.50 (s, keto-CH), 6.79 (s, 2H, C_6H_2), 16.65 (s, 1H, OHO). The percentage of the enol form, determined from a comparison of the integrations of keto CH and enol OHO signals, is 92%.

NMR spectrum $\delta(^{13}C)$: 15.13 (C13), 20.51 (C12 C14), 24.11 (C1 C5), 115.14 (C3), 128.18 (C6), 130.08 (C7 C11), 133.60 134.11 (C8 C10), 136.70 (C9), 190.97 (C2 C4).

The crystal structure was determined on a Picker four-circle diffractometer

TABLE 1

Fractional atomic coordinates for 3-(3',4',5'-trimethylphenyl)-pentane-2,4-dione, $C_{14}H_{18}O_2$

	x	*y*	*z*
C1	0.3757(13)	0.3170(19)	−0.0967(11)
C2	0.1724(11)	0.3087(9)	−0.0653(9)
C3	0.0457(10)	0.2694(8)	0.0647(7)
C4	−0.1383(10)	0.2684(8)	0.0797(8)
C5	−0.2839(12)	0.2324(15)	0.2125(10)
C6	0.1144(8)	0.2374(8)	0.1801(6)
C7	0.1494(9)	0.3561(9)	0.2655(7)
C8	0.2112(8)	0.3319(8)	0.3748(7)
C9	0.2362(8)	0.1790(8)	0.4033(6)
C10	0.2030(8)	0.0571(8)	0.3187(7)
C11	0.1403(9)	0.0870(8)	0.2095(8)
C12	0.2485(13)	0.4673(9)	0.4629(9)
C13	0.3044(12)	0.1486(10)	0.5234(8)
C14	0.2295(14)	−0.1095(9)	0.3446(10)
O1	−0.1955(8)	0.3012(6)	−0.0219(6)
O1	0.1204(8)	0.3438(6)	−0.1693(5)
H	−0.038 (15)	0.327 (12)	−0.125(11)

recently interfaced to an AT-TURBO 286 IBM-compatible microcomputer (full details will be published elsewhere) using Zr filtered Mo$K\alpha$ radiation and pulse-height analysis. The crystal was well formed: dimensions $0.10 \times 0.30 \times 1.0$ mm. The calculation of the least-squares unit-cell dimensions and data collection were done using a modified version of a program written by Grant and Gabe [10].

Crystal data: $C_{14}H_{18}O_2$, RMM 218.30, space group $P\bar{1}$; $a = 7.786(16)$ Å, $b = 8.643(16)$ Å, $c = 10.358(22)$ Å, $\alpha = 90.12(17)^\circ$, $\beta = 73.54(17)^\circ$, $\gamma = 100.83(17)^\circ$; $U = 655.6$ Å^3; $Z = 2$; $D_c = 1.11$ g cm^{-3}, $F(000) = 236$.

Intensity data were collected in θ–2θ scan mode over 2° at 2° per minute. Only non-equivalent reflections were recorded to $2\theta_{max} = 50°$. There were 868 reflections out of 1633 having $I(\text{net}) > 2.5\sigma I(\text{net})$. Structure analysis was carried out using the NRCVAX package [11]. The structure was solved by direct

TABLE 2

Bond lengths and bond angles for 3-(3′,4′,5′-trimethylphenyl)pentane-2,4-dione, $C_{14}H_{18}O_2$

Bond lengths (Å)			
C(1)-C(2)	1.510(3)	C(7)-C(8)	1.380(3)
C(2)-C(3)	1.423(4)	C(8)-C(9)	1.415(3)
C(2)-O(2)	1.309(3)	C(8)-C(12)	1.518(3)
C(3)-C(4)	1.395(3)	C(9)-C(10)	1.403(3)
C(3)-C(6)	1.487(3)	C(9)-C(13)	1.525(3)
C(4)-C(5)	1.503(4)	C(10)-C(11)	1.395(3)
C(4)-O(1)	1.304(2)	C(10)-C(14)	1.527(3)
C(6)-C(7)	1.392(3)		
C(6)-C(11)	1.400(3)		
Bond angles (°)			
C(1)-C(2)-C(3)	124.4(2)	C(7)-C(8)-C(12)	120.1(1)
C(1)-C(2)-O(2)	113.8(2)	C(9)-C(8)-C(12)	121.3(1)
C(3)-C(2)-O(2)	121.7(2)	C(8)-C(9)-C(10)	119.8(1)
C(2)-C(3)-C(4)	118.4(2)	C(10)-C(9)-C(13)	120.3(1)
C(2)-C(3)-C(6)	119.1(2)	C(9)-C(10)-C(11)	119.5(1)
C(4)-C(3)-C(6)	122.5(2)	C(9)-C(10)-C(14)	121.7(1)
C(3)-C(4)-C(5)	123.2(2)	C(11)-C(10)-C(14)	118.8(1)
C(3)-C(4)-O(1)	121.7(2)	C(6)-C(11)-C(10)	121.5(1)
C(5)-C(4)-O(1)	115.2(2)	C(3)-C(6)-C(7)	120.6(1)
C(3)-C(6)-C(11)	121.7(1)	C(7)-C(6)-C(11)	117.7(1)
C(6)-C(7)-C(8)	122.9(1)	C(7)-C(8)-C(9)	118.7(1)
Dihedral angle between the enol and 3,4,5-trimethylphenyl rings 85°			
Hydrogen bond	(*Å*)		(°)
O(1)-O(2)	2.460(3)	O(1)-H-O(2)	153.4
O(1)-H	1.361		
O(2)-H	1.166		

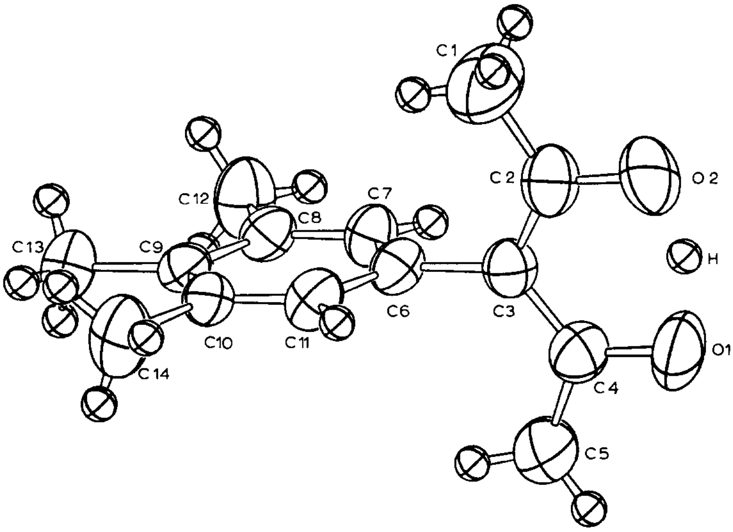

Fig. 1. Diagram of 3-(3′,4′,5′-trimethylphenyl)-pentane-2,4-dione showing atom-labelling scheme.

methods using the routine SOLVER of the above package. Anisotropic least-squares refinement was uneventful. Most hydrogen atoms were found on the final DF map and, apart from the hydrogen bonded hydrogen atom, were given idealized positions (C–H = 1.0 Å) with isotropic B_{eq} values equal to those of the atoms to which they were attached. The final $R_f = 0.061$, and with weights from counting statistics gave $R_w = 0.064$. Atomic coordinates are listed in Table 1, and bond lengths and angles in Table 2. An ORTEP [12] plot of the molecule is given in Fig. 1. Non-hydrogen atom isotropic temperature factors, and selected non-bonded distances are available as supplementary data*.

DISCUSSION

The *enol* tautometers of the β-diketones have an intramolecular hydrogen bond that is loosely described as strong, and about which there has been a continuing debate [2]. For a long time the issue was over the symmetry of the hydrogen bond and whether the proton was centred between the two oxygen atoms in **Ie**. Recent studies that we have carried out on pentane-2,4-dione derivatives substituted at the 3-position, have shown that the bonds are short with $R_{O \cdots O} < 2.45$ Å and that the change in chemical shift on deuteriation [$\Delta\delta$(H–D)], is positive [6–8]. These data have been taken to mean that, although the hydrogen bond has a double-minimum potential-energy well, the

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proton sits above the internal energy barrier but the deuteron is still confined to one of the wells.

The structure of $C_{14}H_{18}O_2$ shows that the steric leverage on the oxygens of the hydrogen bond, that we had hoped for, has not been achieved. The hydrogen bond length, $R_{O\cdots O}$ is 2.460 Å, very similar to other 3-substituted phenyl derivatives which have the following $R_{O\cdots O}$ values: 4′-$NO_2C_6H_4$–, 2.445 Å [7]; 4′-$MeOC_6H_4$–, 2.449 Å [6]; 4′-PhC_6H_4–, 2.441 Å [8]; 4′-$PhOC_6H_4$–, 2.443 Å [7]; and 4′-$Me_2CHC_6H_4$–, 2.419 Å [7]. If anything, the extra substituents on the phenyl ring of the 3′,4′,5′-trimethyl derivative have made the hydrogen bond slightly longer. Clearly these compounds have the kind of hydrogen bonding classed as strong [2]. The conclusion is that neither electronic effects within the molecule, nor steric effects across the molecule have much effect on the hydrogen bonding.

It may be that the three methyl groups did not exert any leverage. The steric effect of the three adjacent methyl groups is to cause an opening of the external angles from 120° to 121.3(6)° and 121.8(6)° for C(9)–C(8)–C(12) and C(9)–C(10)–C(14), respectively. There is a consequent reduction in the internal angles at C(8) and C(10) and opening at the two atoms bearing hydrogen, C(7) and C(11), suggesting a mechanical transmission of the strain. Similar distortions have been reported in 3,4,5-trimethylbenzoic acid [13], and larger distortions in the same sense have been observed in 2,6-di-t-butyl-4-methyl phenol [14], in which the substitution pattern is the same but the steric bulk of the substituents is larger.

The proton of the hydrogen bond is slightly asymmetrically placed with $R_{O\cdots H}=1.166$ and 1.361 Å, similar to that found between formate ions in potassium hydrogen formate [15]. In this latter compound $R_{O\cdots O}$ is 2.437 Å, and the system has a perfectly linear OHO bond with $R_{O\cdots H}$ distances of 1.167 and 1.270 Å. The sensitivity of the proton to crystal forces has been investigated by Misaki and co-workers [15–17] for the anions [$(p\text{-Me-}C_6H_4CO_2)_2H^+$] and [$(p\text{-Br-}C_6H_4CO_2)_2H^+$] in lattices with a variety of counter cations. The hydrogen bond lengths $R_{O\cdots O}$ were found to range from 2.445 to 2.538 Å, and the symmetry of the bond was likewise variable. These workers concluded that lattice forces are paramount in determining the geometry of a hydrogen bond. Were that also to be the case with β-diketones, this might then explain the variations in symmetry around the enol ring which have given rise to the idea of "resonance-assisted hydrogen bonding" [18].

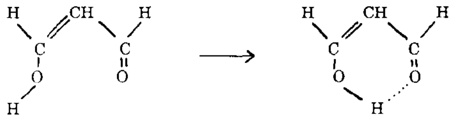
If the proton in the hydrogen bond is above the internal energy barrier of the potential energy well between the two oxygen atoms, then its location should be centred between them, assuming the rest of the molecule has C_{2v} symmetry. Given an angle $\angle OHO=153°$ then each $R_{O\cdots H}$ should be 1.26 Å. The rest of the enol ring system is almost symmetrical with the bond $R_{C\text{-}O}=1.309$ and 1.304 Å, and the $R_{C\text{-}C}=1.423$ and 1.395 Å. Perfect C_{2v} symmetry is not achieved since the dihedral angle between the enol and phenyl rings is not exactly 90°, but 85°. This distortion may be due to steric forces within the molecule itself, but probably arises from local lattice forces. In the gas phase or in a non-polar solvent then we might expect the molecule to achieve the highest symmetry and the enol hydrogen bond to be perfectly centred.

Recently Gilli et al. [19] have used the asymmetry of the enol ring to define a parameter Q. This is composed of q_1 and q_2, which are the differences in $R_{C\text{-}O}$ and $R_{C\text{-}C}$, respectively, for the two halves of the ring. In the case of $C_{14}H_{18}O_2$, $q_1=0.014$ Å and $q_2=0.013$ Å, making $Q=0.027$ Å. In the paper by Gilli et al. [19], systems with the enol fragment, H–O–C=C–C=O, were found to have Q values ranging from almost zero up to 0.12 Å, and this quantity was found to relate to other hydrogen bond parameters such as overall bond length. A value of 0.027 Å would be consistent with resonance stabilized hydrogen bonding.

The downfield chemical shift $\delta(^1H)$ of the enol proton of $C_{14}H_{18}O_2$ at 16.65 reveals little about the strength of the hydrogen bond. The other substituted pentane-2,4-diones have values ranging from 15.40 to 18.50 for this parameter, but no correlation with the electron releasing or withdrawing effects of the α-substituents could be found [7]. The farthest downfield chemical shift for the hydrogen bonding proton in these compounds is 21.44 for a protonated 1,3-diphenyl-2-methylpropane-1,3-dione in HBr/CF_2Br_2, but this ionic species has a negative deuterium isotopic shift in the NMR indicating a very strong hydrogen bond [26].

The ^{13}C NMR spectrum shows only a single carbonyl resonance. Solid state NMR spectra of β-diketones reveals two carbonyl signals where the hydrogen bond is asymmetric, as with the 4′-$Me_2CHC_6H_4$-derivative which has $\delta(^{13}C)$ of 187.1 and 194.4 [27].

If the hydrogen bonding itself is the driving force behind the structure of the β-diketone enols, and is relatively unaffected by electronic or steric factors, then we need to know its innate strength. The hydrogen bond energy, E(OHO), is defined as the difference in energy between the open and closed enol forms, and attempts have been made to calculated this by ab initio methods for the model compound malondialdehyde in both forms (**IIo** and **IIc**):



IIo IIc

The value obtained was 75 kJ mol^{-1} [19], although an earlier theoretical investigation gave a value of 97 kJ mol^{-1} [20].

Since there is no easy way in which this energy difference can be measured directly, the best resource is to the well-tested linear correlation between the hydrogen bond energy and the IR shift $\Delta\nu_{OH}$. This relationship was proposed many years ago [21], and continues to be used, and confirmed as valid [22]. For our purposes to obtain $\Delta\nu_{OH}$ we need to know the stretching vibration of the open enol ν_{OH} (**IIo**), as well as the hydrogen bonded form (**IIc**).

In the IR spectrum of $C_{14}H_{18}O_2$ in dilute solutions there is no band corresponding to ν_{OH} of the open form. However, in pentane-2,4-dione itself this band has been identified at ca. 3600 cm^{-1} [23], and we have every expectation that for $C_{14}H_{18}O_2$ it would be within 100 cm^{-1} of this. In the IR spectrum of β-diketones a broad band with its maximum lying between 1475 and 1450 cm^{-1} has been identified as ν_{OHO} [24] and in the IR spectrum of $C_{14}H_{18}O_2$ a band at 1500 cm^{-1} is assigned to this mode, giving a $\Delta\nu_{OH}$ of 2100 ± 100 cm^{-1}. In recent work on the strong hydrogen bonds of the XHY^- species ($X,Y = F$, Cl, Br or CN) [25] a shift of 2100 cm^{-1} would correspond to an average hydrogen bond energy of 110 ± 10 kJ mol^{-1}.

If the hydrogen bond energy of these β-diketones were in excess of 100 kJ mol^{-1} then it would explain the preponderance of the enol form. In earlier papers on aryl substituted pentane-2,4-dione we found no evidence of the keto–enol equilibrium in solutions [6,7], except for *p*-diphenyl [8] which had 1.5% of the keto form. The present compound reveals 8% of the keto form in $CDCl_3$, almost the same as that of pentane-2,4-dione in this solvent. This is hard to rationalise with the strength and symmetry of the hydrogen bond. Clearly, the forces operating on these systems (electronic, steric, solvent or lattice) are finely balanced.

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