β-Diketone Interactions Part 8.[1] The Hydrogen Bonding of the Enol Tautomers of Some 3-Substituted Pentane-2,4-diones

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Three new derivatives of pentane-2,4-dione (PD) have been synthesized: 3-(4-nitrophenyl), 3-(4-phenoxyphenyl) and 3-(4-isopropylphenyl). The *X*-ray crystal structures of these compounds show them to have very short hydrogen bonds with $R(\mathrm{O}\cdots\mathrm{O})$ = 2.445, 2.443, and 2.419 Å, respectively. Those parameters most sensitive to hydrogen bonding—^{1}H chemical shift, change in chemical shift on deuteriation [$\Delta\delta(\mathrm{H,D})$], and stretching frequencies [$\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{max.}}(\mathrm{OHO})$]—have been measured for these, and other 3-derivatives of PD, with a view to probing the potential energy well of this type of bond. The conclusion is that in all of the compounds with $R(\mathrm{O}\cdots\mathrm{O}) < 2.45$ Å, the hydrogen bonding is very strong with the proton zero point energy above the internal barrier.

Strong hydrogen bonds are mostly to be found between molecules and ions.[2] However, the enol tautomers of the β-diketones offer rare examples of strong hydrogen bonds in a neutral environment.[3] Pentane-2,4-dione (PD) itself has only a moderately strong bond judged by its $R(\mathrm{O}\cdots\mathrm{O})$ of 2.535 Å, which was measured when this molecule fortuitously turned up in crystals of a drug complex.[4] On the other hand, the few 3-substituted derivatives of PD whose structures have been analysed, show OHO bonds significantly shorter than this,[1,5–7] with $R(\mathrm{O}\cdots\mathrm{O})$ below 2.45 Å, establishing them as very strong hydrogen bonds.[2]

The shape of the potential energy well between the two heavier nuclei determines the class of hydrogen bond.[3] The height of the barrier between the two minima falls as the nuclei approach each other, and this is reflected in the parameter $\Delta\delta(\mathrm{H,D})$.[8,9] In choosing 3-substituted PD compounds we hoped to study the relationship between $R(\mathrm{O}\cdots\mathrm{O})$ and $\Delta\delta(\mathrm{H,D})$ over the transition from strong to very strong hydrogen bonds, *i.e.* the case 3–case 4 boundary.[3] Case 3 hydrogen bonds have the proton above the potential energy barrier but the deuteron trapped within one of the wells; case 4 hydrogen bonds have both proton and deuteron above the barrier. In the former, $\Delta\delta(\mathrm{H,D})$ is positive (upfield shift on deuteriation), whereas in the latter it is negative.

We now report the structures and properties of three new crystalline derivatives of PD. All are *para* substituted phenyl compounds, these being chosen because they offer a variety of electronic effects, and they form crystals suitable for *X*-ray structural analysis.

Experimental

Instruments.—I.r. spectra were recorded on a PE 983G spectrometer and n.m.r. spectra on Bruker WM250 and AM360 spectrometers (^{1}H at 250 and 360 MHz, ^{2}H at 38.4 MHz). Crystal structures were determined on an Enraf–Nonius CAD-4 diffractometer.

3-(4-*Nitrophenyl*)-*PD* (**1**).—4-Nitrophenylacetone was prepared by the method of Overberger and Biltech,[10] by decarboxylation of diethyl 4-nitrophenylmalonate, obtained from 4-nitrophenylacetyl chloride and diethyl malonate. A solution of 4-nitrophenylacetone (2.27 g, 12.7 mmol) and acetic anhydride (2.5 g, 24.5 mmol), dissolved in dry diethyl ether, was added to an ether solution of BF_3 (4 g $BF_3\cdot OEt_2$, 28 mmol) at 0 °C. The mixture was stirred for 4 h, and allowed to attain room temperature. BF_3 was hydrolysed by refluxing with aqueous sodium acetate solution. The mixture was cooled and extracted with ether. The organic phase was neutralized with saturated $NaHCO_3$ solution, separated, dried ($MgSO_4$) and stripped of solvent to yield a yellow solid which was recrystallized from methanol to give 3-(4-*nitrophenyl*)-*PD* (0.95 g, 34%), m.p. 108–110 °C (Found: C, 59.9; H, 5.0; N, 6.3. $C_{11}H_{11}NO_4$ requires: C, 59.7; H, 5.0; N, 6.3%), $\nu_{\mathrm{max.}}$ 3 103w, 3 080w, 2 930w, 2 840w, 1 950w, 1 594vs, 1 520vs ($\nu_{\mathrm{as}}NO_2$), 1 414s, 1 400vs, 1 347vs ($\nu_{\mathrm{s}}NO_2$), 1 330s, 1 315s, 1 262m, 1 232m, 1 104s, 1 020m, 998sbr, 915s, 853s, 756m, 718w, 703s, 650w, 624w, 551m, 480w, 452m, 418w, and 322w cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}; δ_{H} 1.91 (s, 6 H, MePD), 7.38, 7.41, 8.26, 8.29 (dd, 4 H, benzeneCH), and 16.78 (s, 1 H, OHO).

3-(4-*Phenoxyphenyl*)-*PD* (**2**).—4-Phenoxyphenyl-lead triacetate was prepared by the method of De Vos *et al.*[11] Diphenyl ether (20.4 g, 0.12 mol) was added slowly to a solution of lead tetra-acetate (10 g, 22.4 mmol) and dichloroacetic acid (11 g, 85 mmol) in benzene. The solution was stirred for 30 min, extracted with water to remove unchanged lead compound and filtered through Celite. The addition of hexane gave the plumboxane. This was twice stirred with solutions of acetic acid in $CHCl_3$ for 1 h, extracted with water, then hexane added to release 4-phenoxyphenyl-lead triacetate, which crystallized when allowed to stand overnight at 5 °C.

The triacetate was converted into 3-(4-*phenoxyphenyl*)-*PD* using the method of Pinhey and Rowe.[12] 4-Phenoxyphenyl-lead triacetate (4 g, 7.2 mmol) was added to a $CHCl_3$ solution of PD (0.8 g, 8.0 mmol) and pyridine (1 cm^3). The mixture was stirred at 40 °C for 24 h, diluted with $CHCl_3$ and extracted with water (20 cm^3) and twice with sulphuric acid (20 cm^3; 3 mol dm^{-3}). The acid and aqueous washings were extracted with $CHCl_3$ and all the combined $CHCl_3$ phases were washed, dried ($MgSO_4$), and stripped of solvent and the product recrystallized from methanol to give pale yellow crystals of 3-(4-*phenoxyphenyl*)-*PD* (0.96 g, 3.6 mmol, 50%) (Found: C, 76.1; H, 6.0. $C_{17}H_{16}O_3$ requires C, 76.1; H, 5.95%), $\nu_{\mathrm{max.}}$ 2 923w, 1 586vs, 1 488vs, 1 410s, 1 335vs, 1 231vs, 1 162vs, 1 099s, 1 075s, 1 022s, 1 000sbr, 919m, 871s, 845s, 780m, 757vs, 735m, 693s, 607w, 590m, 551m, 498m, 460m, 396w, and 360w cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}); δ_{H}

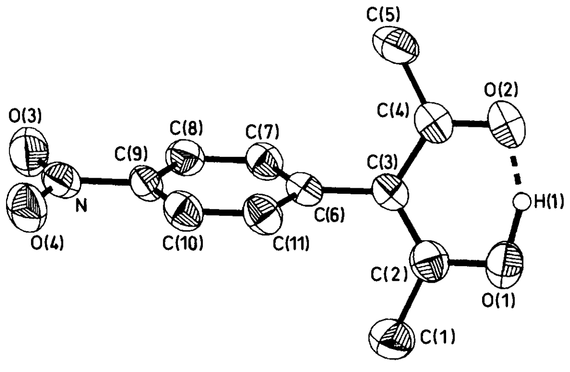

Figure 1. The molecular structure and numbering scheme of 3-(4-nitrophenyl)pentane-2,4-dione (**1**). For clarity only the refined enol hydrogen atom is shown and this is drawn with an arbitrary radius.

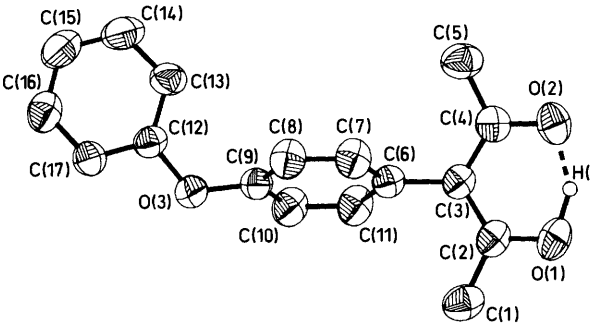

Figure 2. The molecular structure and numbering scheme of 3-(4-phenoxyphenyl)pentane-2,4-dione (**2**). For clarity only the enol hydrogen atom is shown and this is drawn with an arbitrary radius.

1.93 (s, 6 H, MePD), 7.00–7.40 (complex region, 9 H, benzene CH), and 16.68 (s, 1 H, OHO).

3-(4-*Isopropylphenyl*)-*PD* (**3**).—4-Isopropylphenyl-lead triacetate was prepared by the method of Bell *et al.*[13] Cumene (20 cm^3) was added to a $CHCl_3$ solution of lead tetra-acetate (10 g, 22.4 mmol) and trichloroacetic acid (15 g, 90 mmol). When all the lead salt had dissolved the solution was washed with water and filtered through Celite. Hexane was added to precipitate the plumboxane. This was stirred in a $CHCl_3$ solution of acetic acid for 1 h, washed and stirred again with acetic acid for 1 h. The solution was washed, hexane added, and the triacetate precipitated. This was then treated with PD (0.4 g, 4 mmol) in the manner described for 3-(4-*phenoxyphenyl*)-*PD*, and gave crystals of 3-(4-*isopropylphenyl*)-*PD* (0.54 g, 2.0 mmol, 49%) m.p. 69–71 °C (Found: C, 73.2; H, 8.1 $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%), $\nu_{max.}$ 3 006m, 2 969m, 2 925m, 2 573wbr, 2 329wbr, 1 608vsbr, 1 475sh, 1 404vs, 1 330sh, 1 261vs, 1 021sbr, 996s, 912s, 678m, 630w, 541m, 483m, 400w, 369m cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}); δ_H 0.07 (s, 6 H, Me_2CH), 1.28 (d, 6 H, MePD), 2.32 (septet, 1 H, CH), 7.30 (m, 4 H, benzene-CH), and 16.67 (s, 1 H, OHO).

3-(4-*Methylphenyl*)-*PD*.—This compound was made in a similar manner to (**3**) starting with 4-methylphenyl-lead triacetate. The product, 3-(4-methylphenyl)-PD, was obtained as a crystalline material (50%), m.p. 72–74 °C (lit.,[12] 75–76 °C) (Found: C, 75.4; H, 7.4. Calc. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4%); $\nu_{max.}$ 3 010vs, 2 980vs, 2 860s, 2 590w, 2 350w, 2 300w, 1 898m, 1 606vs, 1 510vs, 1 410vs, 1 330vs, 1 260sh, 1 182m, 1 104m, 994vs, 920m, 816vs, 724m, 657w, 556s, and 444m cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}); δ_H 1.89 (s, 6 H, MePD), 2.38 (s, 3 H, phenyl-Me), 7.05 (d, 2 H, benzeneCH), 7.19 (d, 2 H, benzene-CH), and 16.66 (s, 1 H, OHO).

Crystals of this compound were submitted to *X*-ray analysis but gave a final *R* of 0.15, and consequently are not reported in detail.

Tetra-acetylethane.—This was prepared from PD and the sodium salt of PD, in methanol, according to the method of Charles[14] (44%), m.p. 191–192 °C (lit.,[14] 192–193 °C) (Found: C, 60.1; H, 7.2 Calc. for $C_{10}H_{14}O_4$: C, 60.6; H, 7.1%), $\nu_{max.}$ 3 005w, 2 970w, 2 927w, 2 331wbr, 1 596vs, 1 520sh, 1 407vsbr, 1 362s, 1 251sbr, 1 020s, 996s, 912s, 678w, 544m, 483m, 400w, 370w cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}); δ_H 2.02 (s, 12 H, MePD) and 16.78 (s, 2 H, OHO).

3,3′-*Dithiobis*-(*PD*).—A solution of disulphur dichloride (6.75 g, 50 mmol) in CCl_4 was added slowly to PD (10 g, 0.1 mol) and stirred until a solid mass formed which was recrystallized from acetone to give pale brown crystals of 3,3′-*dithiobis*-(*PD*) (11.0 g, 37 mmol, 75%) m.p. 74–76 °C (lit.,[15] 90–92 °C) (Found: C, 45.5; H, 5.2; S 24.8 Calc. for $C_{10}H_{14}O_4S_2$: C, 45.8; H, 5.3; S, 24.4%), $\nu_{max.}$ 3 010w, 2 960w, 2 920w, 2 600wbr, 1 910wbr, 1 565vs, 1 500sh, 1 404vsbr, 1 340s, 1 250m, 1 015s, 906s, 650m, 532m, 472m, 445m, 400w, and 380w cm^{-1} (the region 1 700–1 100 is overlaid by an intense continuum centred at *ca.* 1 500 cm^{-1}); δ_H 2.38 (s, 12 H, MePD) and 17.06 (s, 2 H, OHO). The ^1H n.m.r. spectrum was also run in highly polar solvents, namely [$^2H_6$]DMSO, [$^2H_3$]MeCN, and DMF, but in all cases only signals of the enol tautomer were observed.

Crystallography.—Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[16] using a CAD-4 diffractometer operating in the ω–2θ scan modes, with Ni-filtered Cu-K_α radiation (λ = 1.5418 Å), for (**1**) and graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å) for (**2**) and (**3**). The relevant experimental data are summarized in Table 1.

The structures were solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Methyl, isopropyl, and phenyl hydrogen atoms were placed in calculated positions (C–H 0.96 Å, U = 0.10 Å^2). Enolic hydrogen atoms for (**1**) and (**2**) were allowed unrestricted isotropic refinement. Although these enol hydrogen atoms refined to chemically feasible positions (see Table 5), their isotropic thermal parameters are high (see Tables 2 and 3), which suggests that these hydrogen atoms may not be fully localized, as indicated by Figures 1 and 2, and that there is dynamic fluctuation of these hydrogens between the enolic oxygens. Indeed, the short O···O separations and similar C–O bond lengths strongly suggest this to be the case (see Table 6). However, one of the more dominant hydrogen bonding forms may be depicted here. For (**3**), a final difference Fourier map revealed a small peak, 0.16 e Å^{-3}, mid-way between the enolic oxygen atoms. However, the smallness of the peak, and the poor quality of data for (**3**), precluded its refinement as an enol hydrogen atom.

All calculations were performed with the SHELX-76[17] and SHELX-86[18] packages of crystallographic programs. Atom co-ordinates are given in Tables 2–4, and selected bond lengths and angles in Table 5. The structures and atom labelling are shown in Figures 1–3. Non-hydrogen atom anisotropic temperature factors, hydrogen fractional atomic co-ordinates

Table 1. Crystal data, details of intensity measurements and structure refinement for 3-(4-nitrophenyl)pentane-2,4-dione (**1**), 3-(4-phenoxyphenyl)pentane-2,4-dione (**2**), and 3-(4-isopropylphenyl)pentane-2,4-dione (**3**).

	(1)	**(2)**	**(3)**
Formula	$C_{11}H_{11}NO_4$	$C_{17}H_{16}O_3$	$C_{14}H_{18}O_2$
M	221.21	268.31	218.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/a$
a/Å	10.249(1)	8.824(3)	10.234(9)
b/Å	7.621(1)	15.634(4)	11.587(5)
c/Å	13.525(2)	10.700(5)	11.190(2)
B/°	90.21(1)	105.15(3)	99.75(4)
U/Å^3	1 056.4(2)	1 424.8(9)	1 308(1)
Z	4	4	4
D_c/g cm^{-3}	1.391	1.251	1.109
F(000)	464	568	472
μ/cm^{-1}	8.6	0.8	0.7
θ range	$6 \leqslant 2\theta \leqslant 150°$	$3 \leqslant 2\theta \leqslant 50°$	$3 \leqslant 2\theta \leqslant 50°$
h, k, l range	$-12 \rightarrow 12; 0 \rightarrow 9; 0 \rightarrow 16$	$0 \rightarrow 10; 0 \rightarrow 18; -12 \rightarrow 12$	$0 \rightarrow 12; 0 \rightarrow 13; -13 \rightarrow 13$
Intensity variations (%)	<3%	<3%	<3%
Total no. reflections	2 442	2 794	2 573
No. unique reflections	2 173	2 509	2 298
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
No. reflections used in the refinement	1 269	1 829	1 226
No. refined parameters	155	191	157
Max. least-squares shift-to-error ratio	0.07	0.15	0.35
Min. and max. height in final difference Fourier map(Δρ/e Å^{-3})	−0.24, 0.20	−0.24, 0.17	−0.31, 0.24
Function minimized	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme parameter g in $w = 1/[\sigma^2(F_o) + gF^2{}_o]$	0.0001	0.001	0.001
Final R	0.054	0.061	0.095
Final R_w	0.045	0.073	0.111

Table 2. Fractional atomic co-ordinates (× 10^4) for 3-(4-nitrophenyl)-pentane-2,4-dione (**1**).

	x	y	z
O(1)	1 099(2)	4 747(3)	6 879(2)
O(2)	539(2)	2 158(3)	5 898(2)
O(3)	5 721(3)	−3 257(3)	9 609(2)
O(4)	4 418(2)	−2 592(3)	10 805(2)
N	4 759(3)	−2 493(4)	9 942(2)
C(1)	2 439(4)	4 691(5)	8 293(3)
C(2)	1 767(3)	3 724(5)	7 471(2)
C(3)	1 845(3)	1 937(4)	7 324(2)
C(4)	1 200(3)	1 197(5)	6 481(2)
C(5)	1 268(3)	−720(4)	6 254(3)
C(6)	2 596(3)	782(4)	8 014(2)
C(7)	3 727(3)	−51(4)	7 699(2)
C(8)	4 432(3)	−1 134(4)	8 324(2)
C(9)	3 996(3)	−1 349(4)	9 276(2)
C(10)	2 883(3)	−559(4)	9 617(2)
C(11)	2 182(3)	519(4)	8 987(2)
H(1)	617(45)	3 781(63)	6 347(33)

and isotropic temperature factors are available on request from the Cambridge Crystallographic Data Centre.*

Table 3. Fractional atomic co-ordinates (× 10^4) for 3-(4-phenoxyphenyl)-pentane-2,4-dione (**2**).

	x	y	z
O(1)	10 843(2)	5 713(1)	3 642(2)
O(2)	11 221(2)	4 171(1)	3 933(2)
O(3)	2 141(2)	4 381(1)	1 051(2)
C(1)	8 408(3)	6 379(2)	2 796(3)
C(2)	9 356(3)	5 588(2)	3 170(2)
C(3)	8 709(3)	4 761(2)	3 045(2)
C(4)	9 738(3)	4 062(2)	3 469(2)
C(5)	9 179(4)	3 164(2)	3 427(3)
C(6)	6 992(3)	4 624(2)	2 529(2)
C(7)	6 374(3)	4 197(2)	1 374(3)
C(8)	4 777(3)	4 077(2)	884(3)
C(9)	3 759(3)	4 401(2)	1 542(3)
C(10)	4 336(3)	4 830(2)	2 690(3)
C(11)	5 934(3)	4 936(2)	3 180(3)
C(12)	1 350(3)	3 623(1)	649(2)
C(13)	1 974(3)	2 828(2)	1 035(3)
C(14)	1 055(4)	2 120(2)	606(3)
C(15)	−447(3)	2 196(2)	−175(3)
C(16)	−1 040(3)	2 994(2)	−534(3)
C(17)	−143(3)	3 710(2)	−127(2)
H(1)	11 387(46)	5 074(35)	3 905(42)

Discussion

The changes in the properties of PD caused by substitution at the 3-position are difficult to predict,[3,19] This is exemplified by the extent of enolization, which ranges for 0.2% enol for the 3-isopropyl derivative to 100% enol with 3-cyano,[20] 3-methoxycarbonyl,[21] 3-methylthio,[22] and 3-(4-methoxyphenyl)[7] substituents. We now report three new crystalline derivatives of PD, substituted at the 3-position by 4-isopropyl-, 4-nitro- and 4-phenoxyphenyl groups, and these too display only the enol tautomer, both in the solid state and in solution. This is one indication that the hydrogen bonding is strong, and may even be centred (**I**). *X*-Ray analysis supports this and allows a fresh insight into n.m.r. and i.r. data.

Bond Lengths.—It is shown that substituted derivatives of PD have stronger hydrogen bond by their shorter $R(\mathrm{O}\cdots\mathrm{O})$ distances of less than 2.45 Å compared with that of PD itself

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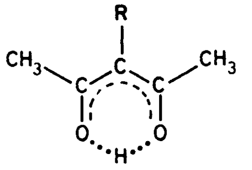
* For details see Instructions for Authors, *J. Chem. Soc., Perkin Trans 2,* 1989, Issue 1.



(I)

(2.535 Å). Short bonds have been reported for 4- methoxyphenyl-PD,[7] 3,3′-trithiobis(PD)[5] and tetra-acetylethane, *i.e.* 3,3′(bis(PD).[6] There are now eight PD derivatives for which *X*-ray structural data are available (see Table 6).

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for 3-(4-isopropylphenyl) pentane-2,4-dione (**3**).

	x	*y*	*z*
O(1)	3 175(5)	4 992(4)	5 310(4)
O(2)	1 550(5)	6 056(4)	6 203(3)
C(1)	3 268(7)	4 982(7)	3 194(7)
C(2)	2 636(6)	5 371(5)	4 232(5)
C(3)	1 544(5)	6 102(4)	4 106(4)
C(4)	1 013(6)	6 394(5)	5 143(4)
C(5)	−178(8)	7 128(7)	5 081(6)
C(6)	924(5)	6 532(4)	2 893(4)
C(7)	1 197(6)	7 630(4)	2 506(4)
C(8)	553(7)	8 035(5)	1 391(5)
C(9)	−351(6)	7 392(5)	632(4)
C(10)	−608(6)	6 294(5)	1 008(5)
C(11)	20(6)	5 893(5)	2 110(5)
C(12)	−1 064(8)	7 855(7)	−564(5)
C(13)	−2 022(7)	8 798(6)	−416(6)
C(14)	−389(10)	7 891(10)	−1 504(6)

The transition from normal to strong hydrogen bonding is marked by the lowering of the internal energy barrier of the potential energy well to below the zero point energy of the hydrogen atom. When this occurs in the enol tautomers of β-diketones the distinction between the carbonyl and enol C–O bonds is lost, and this should be revealed in the structure of the molecule. Table 6, in which this data is tabulated, shows that it has occurred for 3-(biphenyl-4-yl)-PD and 3-(4-phenoxyphenyl)-PD, and probably for the others as well. In PD itself the difference between these two bonds is 0.1 Å, whereas for all the substituted derivatives it is 0.04 Å, with the exception of 3,3′-trithiobis(PD) where the difference is 0.06 Å. Whether the proton is above or below the internal barrier should be reflected in the chemical shift, δ_{OHO}, of the proton.

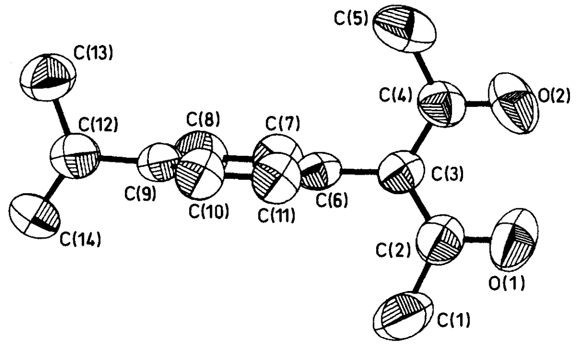


Figure 3. The molecular structure and numbering scheme of 3-(4-isopropylphenyl)pentane-2,4-dione (**3**). For clarity none of the hydrogen atoms are shown. The enol hydrogen atom was not refined.

Table 5. Selected bond lengths and angles for 3-(4-nitrophenyl)- (**1**), 3-(4-phenoxyphenyl)- (**2**) and 3-(4-isopropylphenyl)-pentane-2,4-dione (**3**).

(i) Bond lengths/Å

(**1**)		(**2**)		(**3**)	
C(2)–O(1)	1.309(5)	C(2)–O(1)	1.292(4)	C(2)–O(1)	1.315(7)
C(4)–O(2)	1.270(4)	C(4)–O(2)	1.284(4)	C(4)–O(2)	1.281(7)
C(2)–C(1)	1.499(5)	C(2)–C(1)	1.487(5)	C(2)–C(1)	1.492(9)
C(3)–C(2)	1.379(5)	C(3)–C(2)	1.406(4)	C(3)–C(2)	1.390(9)
C(4)–C(3)	1.432(5)	C(4)–C(3)	1.418(4)	C(4)–C(3)	1.404(8)
C(5)–C(4)	1.495(5)	C(5)–C(4)	1.485(5)	C(5)–C(4)	1.478(10)
C(6)–C(3)	1.495(5)	C(6)–C(3)	1.487(4)	C(6)–C(3)	1.484(7)
H(1)–O(1)	1.14(5)	H(1)–O(1)	1.11(5)		
H(1)–O(2)	1.38(5)	H(1)–O(2)	1.42(6)		
C(9)–N	1.475(5)	C(9)–O(3)	1.387(4)	C(12)–C(9)	1.510(9)
N–O(3)	1.232(4)	C(12)–O(3)	1.386(4)	C(13)–C(12)	1.496(10)
N–O(4)	1.222(4)			C(14)–C(12)	1.354(10)

(ii) Bond angles/°

(**1**)		(**2**)		(**3**)	
C(1)–C(2)–O(1)	113.5(4)	C(1)–C(2)–O(1)	114.9(3)	C(1)–C(2)–O(1)	116.3(7)
C(3)–C(2)–O(1)	122.0(4)	C(3)–C(2)–O(1)	121.4(3)	C(3)–C(2)–O(1)	120.1(7)
C(3)–C(2)–C(1)	124.5(4)	C(3)–C(2)–C(1)	123.6(3)	C(3)–C(2)–C(1)	123.6(6)
C(4)–C(3)–C(2)	118.5(4)	C(4)–C(3)–C(2)	118.0(3)	C(4)–C(3)–C(2)	118.8(6)
C(6)–C(3)–C(2)	121.5(4)	C(6)–C(3)–C(2)	121.1(3)	C(6)–C(3)–C(2)	120.6(6)
C(6)–C(3)–C(4)	120.0(4)	C(6)–C(3)–C(4)	120.8(3)	C(6)–C(3)–C(4)	120.6(6)
C(3)–C(4)–O(2)	120.8(4)	C(3)–C(4)–O(2)	121.6(3)	C(3)–C(4)–O(2)	121.7(7)
C(5)–C(4)–C(2)	117.4(4)	C(5)–C(4)–O(2)	115.7(3)	C(5)–C(4)–O(2)	116.1(6)
C(5)–C(4)–C(3)	121.8(4)	C(5)–C(4)–C(3)	122.7(3)	C(5)–C(4)–C(3)	122.1(6)
H(1)–O(1)–C(2)	103(2)	H(1)–O(1)–C(2)	107(2)		
H(1)–O(2)–C(4)	102(2)	H(1)–O(2)–C(4)	103(2)		
O(2)–H(1)–O(1)	152(4)	O(2)–H(1)–O(1)	149(4)		
O(4)–N–O(3)	123.5(4)	C(12)–O(3)–C(9)	121.5(3)	C(13)–C(12)–C(9)	112.9(6)
C(9)–N–O(3)	118.6(4)			C(14)–C(12)–C(9)	117.8(7)
C(9)–N–O(4)	117.8(4)			C(14)–C(12)–C(13)	119.6(7)

Table 6. Hydrogen bond lengths, carbonyl bond lengths, and chemical shift difference, (H–D), of the enol tautomers of PD and 3-substituted-PDs.

3-Group	R(O ··· O) (Å)	R(C=O) (Å)	R(C–O) (Å)	Δδ(H, D)	Structure ref.
H	2.535	1.238(9)	1.331(9)	+0.61	4
PDS_3	2.461	1.267(17)	1.325(17)	+0.36	5
4-$NO_2C_6H_4$ (**1**)	2.445	1.270(4)	1.309(5)	*n.a.*	This work
4-$MeOC_6H_4$	2.449	1.283(4)	1.301(4)	+0.31	7
4-PhC_6H_4	2.441	1.290(4)	1.292(4)	+0.60	1
PD-*	2.42	1.295(6)	1.310(6)	+0.66	15
4-$PhOC_6H_4$ (**2**)	2.443	1.284(4)	1.294(4)	*n.a.*	This work
4-$Me_2CHC_6H_4$ (**3**)	2.419	1.281(7)	1.315(7)	*n.a.*	This work

* Tetra-acetylethane, *i.e.* 3,3′-bis(pentane-2,4-dione).

Table 7. Chemical shifts of the enol proton of 3-substituted pentane-2,4-diones.

Substituent	σ^{*a}	$\delta_{OHO}{}^{b}$	$\delta_{OHO} - \delta_{OHO}(PD)$	Reference
H	0.49	15.40	0.00	3
Cl	2.96	15.55	0.15	21
CH_3	0.00	16.50	1.10	This work[c]
4-$MeOC_6H_4$	0.60	16.65**	1.25	7
4-MeC_6H_4	0.57	16.66**	1.26	This work
CH_3CH_2	−0.10	16.67**	1.27	This work[d]
4-$Pr^iC_6H_4$	0.56	16.67**	1.27	This work
4-$PhOC_6H_4$	n.a.	16.69**	1.29	This work
4-PhC_6H_4	n.a.	16.72**	1.32	1
4-$NO_2C_6H_4$	1.26	16.78**	1.38	This work
PD[e]	n.a.	16.80**	1.40	This work
CN	3.30	16.90	1.50	21
NO_2	4.25	16.95	1.45	21
PDS_2	n.a.	17.06**	1.66	This work
CH_3S	1.56	17.08	1.68	21
CH_3CO	1.81	17.40	2.00	21
CO_2Me	2.00	17.97	2.57	21
CO_2Et	2.26	18.10	2.70	21
CHO	2.15	18.51	3.11	21

[a] σ* taken from D. D. Perrin, B. Dempsey, and E. P. Sergeant, 'pK_a Prediction for Organic Acids and Bases,' Appendix 1, Chapman and Hall, London, 1981.

[b] Measured in CCl_4 unless indicated ** for $CDCl_3$.

[c] Reported also as 16.35[23] and 17.65.[24]

[d] Reported also as 15.83,[22] 16.80[25], and 17.95 (neat).[24]

[e] Tetra-acetylethane, *i.e.* 3,3′bis(pentane-2,4-dione).

Chemical Shift.—The δ_{OHO} of PDs varies quite markedly with substitution at the 3-position.[1,7,22–26] The values of this parameter have been collected in Table 7 for 18 derivatives. Surprisingly although δ_{OHO} varies over a range of 3.1 p.p.m., there is no correlation of chemical shift or chemical-shift difference, δ_{OHO}–δ_{OHO}(PD), with electron-releasing or withdrawing effects as measured by the Taft σ* parameter. Even the series of 4-substituted phenyl derivatives is not consistent with the expected order of electronic effects.

Indirectly this lack of a relationship is further support for the hydrogen bonding of the β-diketones being on the boundary between class 3 and class 4 strong hydrogen bonds.[3] Steric effects will influence the structure of the PD framework, and this will determine R(O ··· O). As the oxygen atoms approach each other, the internal boundary of the potential energy well decreases, and this in turn determines the location of the proton and consequently its shielding. This chain of cause-and-effect may amplify quite minor changes due to substituents, or alternatively, may even dampen quite major changes. The net result is that δ_{OHO} is unpredictable. The recent report of a chemical shift as far downfield as 21.5 for the enol proton of 2-methyl-1,3-diphenylpropane-1,3-dione-(H^+) is further evidence of this.[27]

Shapet'ko[28] has developed an ingenious theory which predicts the ^1H chemical shift of the hydrogen bonding proton by the addition of β-substituent factors that were calculated empirically. In later papers[28–31] this idea was extended to cover ^{13}C chemical shifts. In all cases the α-substituent was hydrogen. The opportunity to calculate α-substituent factors does not offer itself since derivatives of other β-diketones are few in number. Moreover it seems unlikely that such data will ever be collected since two α-substituted derivatives of 1,3-diphenylpropane-1,3-dione that have recently been reported both exhibit no enol tautomer.[32]

A more significant measure of the type of hydrogen bonding is Δδ(H, D).[33–35] Between case 3 and case 4 hydrogen bonds this inverts in sign from positive to negative. In studying these compounds it was hoped that a trend in Δδ(H, D) would be observed from the +0.61 of PD itself to a value approaching zero as the bond became shorter, with perhaps an inversion to a negative value of Δδ(H, D) for the shortest bond. We were able to measure Δδ(H, D) of PD, 3,3′-dithiobis(PD) and 3,3′-bis(PD), Table 6. Values for 3-(4-methoxyphenyl)-PD and 3-(biphenyl-4-yl)-PD are in the literature,[1,7] but compounds (**1**)–(**3**) resisted several attempts to exchange H with D by recrystallization from MeOD. However, from the limited data of Table 6 we conclude that in all these bonds the zero-point energy of the deuteron remains below the internal energy barrier. The only β-diketone which gives a negative value for Δδ(H, D) is that of 2-methyl-1,3-diphenylpropane-1,3-dione-(H^+) in the strong acid system $HBr–CBr_2F_2$.[27]

Vibrational Modes.—All the i.r. spectra of PD and its derivatives in Table 6 show an intense broad band underlying the region 1 100–1 700 cm^{-1}. Other very strong peaks protrude from this band and these are attributable to $\nu_{C=O}$, $\nu_{C–O}$, and the symmetric and assymetric deformation modes of CH_3. The broad band we believe is the stretching vibration of the hydrogen bond, ν_{OHO}. This assignment is at variance with previous ones which attribute a weak broad band at *ca.* 2 500 cm^{-1} to this mode in 3-substituted PDs.[36–40] On the basis of this interpretation a high energy barrier in the potential energy well was deduced,[40] as indeed would be the case for a weak hydrogen bond which had ν_{OHO} in this region. Since our work shows there to be a low energy barrier this necessitates a reassignment of the i.r. data.

A guide to the expected position of ν_{OHO} can be obtained from R(O ··· O). The simple formula of Bellamy and Owen[41] links the change in ν_{OH} which comes with hydrogen bonding, $\Delta\nu_{OHO}$, with bond length and it has been successfully used by Reedijk *et al.* in assigning the absorption of strong and symmetric hydrogen bonds.[42,43] For PD with a bond length of 2.535 Å and a non-hydrogen bonding ν_{OH} of 3 600 cm^{-1}[44] the formula predicts a value of 2 450 cm^{-1} for ν_{OHO}, slightly lower than observed. For a bond of 2.44 Å the i.r. absorption should come at 1 690 cm^{-1}, near to C=O.

Table 8. Vibrational modes and assignments of the enol tautomers of PD and 3-substituted-PDs.

3-Group	$\nu_{C=O}/cm^{-1}$	ν_{OHO}/cm^{-1}	$\delta_{as}CH_3/cm^{-1}$	δ_sCH_3/cm^{-1}	ν_{C-O}/cm^{-1}	δ'_{OHO}/cm^{-1}
H	1 623	2 640	1 415	1 358	1 251	1 000
$4-Me_2CHC_6H_4$	1 608	1 475	1 404	1 330	1 261	1 021
$4-MeOC_6H_4$	1 602	1 510	1 410	1 330	1 245	974
$4-MeC_6H_4$	1 604	1 510	1 410	1 330	1 260	994
$4-PhOC_6H_4$	1 586	1 488	1 410	1 335	1 231	1 000
$4-PhC_6H_4$[1]	1 596	1 485	1 388	1 330	1 260	980
$4-NO_2C_6H_4$	1 594	1 414	1 400	1 347	1 232	998
PD[a]	1 596	1 500	1 404	1 340	1 250	1 015
$PD-S_2^-$	1 565	1 500	1 404	1 340	1 250	1 015

[a] Tetra-acetylethane, *i.e.* 3,3′-bi(pentane-2,4-dione).

Inspection of i.r. spectra reproduced in the literature[36,45] shows an extreme broadness to the peaks around 1 600 cm^{-1} which is characteristic of strong hydrogen bonding substances,[2] even though the authors chose weak bands at *ca.* 2 500 cm^{-1} for ν_{OHO}. These weak bands we believe are overtones or combinations of ν_{OHO} or δ'_{OHO}.

Better evidence that ν_{OHO} is below 1 600 cm^{-1} came from the spectrum of partially deuteriated 3,3′-dithiobis-(PD). This showed new bands at 1 120 and 740 cm^{-1}, which correspond to a proton equivalence at 1 500 (ν_H/ν_D 1.34) and 1 016 (ν_H/ν_D 1.37) cm^{-1}, which we now assign to the stretching and bending modes of the strong hydrogen bonds.

On this basis we have interpreted the i.r. spectra of the compounds reported here and these are given in Table 8. This lists ν_{OHO} and δ'_{OHO} of the hydrogen bonds, which come around 1 500 and 1 000 cm^{-1} respectively. Also included are the other strong peaks in this region—the methyl deformation modes at *ca.* 1 400 and 1 340 cm^{-1}, and the carbon–oxygen bond vibrations at *ca.* 1 600 ($\nu_{C=O}$) and 1 250 cm^{-1} (ν_{C-O}). The carbonyl peaks were assigned on the basis of their being linearly correlated to δ_{OHO},[22] and in Table 8, where the compounds are listed in order of δ_{OHO}, it can be seen that this relationship is roughly adhered to.

In conclusion it seems that with the introduction of substituents into the 3-position of PD, the hydrogen bonding becomes shorter and stronger. Since a wide variety of electron-donating and -withdrawing groups produce this effect, it seems likely that the reason for a stronger bond is steric in origin. By repelling the β-methyls these substituents will force the enol molecule to relieve steric strain by pushing together the oxygen atoms. This in turn strengthens the hydrogen bond and reduces the energy barrier of the potential energy well. The result is to convert a case 2 hydrogen bond into a strong hydrogen bond (case 3). So far, however, we have not achieved our aim of forcing a neutral enol to become a very strong hydrogen bond (case 4), which would be shown conclusively only by a negative value for δ(H,D). So far this has only been achieved with a protonated enol, *i.e.* β-diketone(H^+).[27]

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