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β-DIKETONE INTERACTIONS

Part 4.* The structures and properties of 1,3-diphenyl-2-methylpropane-1,3-dione, $C_{16}H_{14}O_2$, and 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione, $C_{22}H_{18}O_3$

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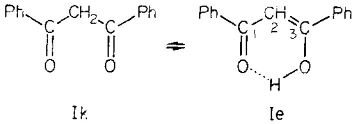
ABSTRACT

The X-ray crystal structures of 1,3-diphenyl-2-methylpropane-1,3-dione and 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione show them both to adopt *cis*-diketo (Z, Z) conformations with carbonyl—carbonyl dihedral angles of 89.0(3)° (2-methyl derivative), and 85.5(4)° and 77.7(4)° for the two molecules in the asymmetric unit of the 2-(4-methoxyphenyl) derivative. These are the first acyclic β-diketones with an α-hydrogen to be reported which do not have an enol configuration in the solid state.

INTRODUCTION

Among the earliest β-diketones to be investigated by X-ray diffraction were the *m*-chloro [1] and *m*-bromo [2] derivatives of 1,3-diphenylpropane-1,3-dione (DPP). That these were in the enol conformation (Ie) was not surprising since the parent compound (DPP) is entirely enol in solution [3, 4].



Ik Ie

Since then several other acyclic β-diketones have been elucidated by X-ray and neutron diffraction and all are enols (see Table 1). In fact the only diketo structure reported is that of pentane-2,4-dione whose electron diffraction determination found the vapour phase to be 66% enol, 34% keto [14]. The

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TABLE 1

Published structural details of β-diketones (X-ray diffraction data unless otherwise indicated)

Group[a]			Form	$R(O\cdot\cdot O)$ (Å)	$R(C_1—O)^b$ (Å)	$R(C_3—O)^b$ (Å)	Ref.
R_1	R_2	R_3					
m-ClC_6H_4	H	m-ClC_6H_4	enol	2.475	1.299	1.318	1
m-BrC_6H_4	H	m-BrC_6H_4	enol	2.464	1.306	1.306	2
Ph	H	Ph	enol	2.460	1.292	1.317	5
Ph	H	Ph[c]	enol	2.463	1.293	1.332	6
Me	H	p-BrC_6H_4	enol	2.481	1.330	1.338	7
Me	H	p-$NO_2C_6H_4$	enol	2.457	1.289	1.306	8
Me	H	Ph	enol	2.498	1.276	1.294	9
Me	H	Ph	enol	2.485	1.279	1.282	10
Me	H	Me	enol	2.535	1.238	1.331	11
Me	$S_3C_5H_7O_2$	Me[d]	enol	2.461	1.267	1.325	12
Me	$CH(COMe)_2$	Me[e]	enol	2.424	1.295	1.302	13

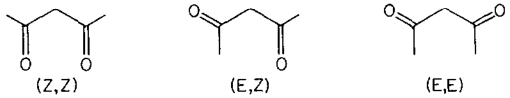
[a] See Ie for numbering. [b] C_1 = carbonyl carbon of Ie; C_3 = C—OH carbon atom of Ie. [c] Neutron diffraction. [d] 3,3'-Titrithiobis(pentane-2,4-dione). [e] Tetraacetylethane, $(MeCO)_2$-$CHCH(COMe)_2$.

keto form had $R(O\cdot\cdot O)$ = 2.767 Å and a dihedral angle of 48.6°; however, the enol tautomer had an unexpectedly short (2.381 Å) and centred hydrogen bond. This was not substantiated by a later solid phase X-ray analysis of pentane-2,4-dione [11].

As part of a continuing investigation into the hydrogen bonding of enol tautomers of β-diketones [15, 16] we have synthesised some 2-substituted derivatives of DPP. The object was to produce sterically hindered molecules that would also crystallise in the enol form but with O••O distances that would categorise them as very strongly hydrogen bonded [17]. To date the shortest such enol hydrogen bond is that of tetracetylethane (2.424 Å) [13].

Attaching substituents at the 2 position of DPP produced the desired crystalline derivatives but their IR spectra showed them to be very different from the parent compound. The expected broad and intense hydrogen bonding absorptions were entirely absent, suggesting these derivatives were entirely in the keto form even in the solid state. Their crystal analysis however offered the opportunity to resolve the conformation of a β-diketone in which the configuration was not predetermined, e.g. by being part of a cyclic system. Three conformers (II) are possible. A recent publication on β-ketocarboxylic esters has shown that the introduction of a mesityl group on the α carbon

II



destabilises the (Z, Z) conformer in favour of the (E, Z) conformer [18]. However there is still hydrogen bonding present between the OH and OR group of the ester so the situation is not strictly comparable to the β-diketones of the kind reported by us.

Ab initio calculations of the model β-diketone $HCOCH_2COH$ (malondialdehyde) have shown the Z, Z conformer to be the lowest energy form, with a carbonyl—carbonyl dihedral angle of 60° [16].

EXPERIMENTAL

IR spectra were run on a Perkin Elmer 983G spectrometer, NMR spectra on a Bruker WM250 instrument (^1H at 250 MHz), and X-ray data were obtained using an Enraf-Nonius CAD-4 diffractometer.

1,3-Diphenyl-2-methylpropane-1,3-dione ($C_{16}H_{14}O_2$)

The potassium salt of DPP was produced from KOH and DPP in ethanol. A sample of this (4.72 g, 18 mmol) was dissolved in DMF (50 cm^3) and excess iodomethane added. The mixture was shaken until neutral, diluted with H_2O (150 cm^3) and extracted several times with C_6H_6. The benzene solution was shaken overnight with dilute hydrochloric acid to remove the *O*-methylated derivative. The product was stripped of solvent and purified by distillation and column chromatography (silica column, 2% ethyl acetate in 40-60 petroleum ether eluant) to yield 1,3-diphenyl-2-methylpropane-1,3-dione (3.0 g, 13 mmol, 70%), m.p. 59—61°C. Found C, 80.02%; H, 5.88%. $C_{16}H_{14}O_2$ requires C, 80.67%; H, 5.88%. ^1H NMR spectrum: 1.55 (d, 3H, CH_3), 5.25 (q, 1H, CH), 7.45 (m, 6H, 6 phenyl CH), 7.90 (m, 4H, 4 phenyl CH) ppm.

1,3-Diphenyl-2-(4-methoxyphenyl)propane-1,3-dione ($C_{22}H_{18}O_3$)

4-Methoxyphenyllead triacetate was synthesised according to the published method [19] from lead tetraacetate and anisole. To a stirred solution of DPP (9.57 g, 75 mmol) and pyridine (20 cm^3, 135 mmol) in $CHCl_3$ (25 cm^3) was added dropwise a solution of 4-methoxyphenyllead triacetate (4.5 g, 9 mmol) in $CHCl_3$ (25 cm^3). After 24 h at 40°C the mixture was washed with water and dilute sulphuric acid. The $CHCl_3$ solution was dried ($MgSO_4$) and stripped of solvent to yield an orange-brown solid that was purified by column chromatography (silica column, 50% ethyl acetate in 40-60 petroleum ether eluant). The yield of 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione was 1.6% (0.4 g, 1.21 mmol), m.p. 150°C (decomp.). Found: C, 79.41%; H, 5.86%. $C_{22}H_{18}O_3$ requires C, 79.98%; H, 5.46%. ^1H NMR spectrum: 3.87 (s, 3H, CH_3O), 6.51 (s, 1H, CH), 7.22—7.92 (m, 14H, 14 phenyl CH).

Infrared spectra

DPP which is 100% enol in the solid, has an IR spectrum dominated by the carbon—oxygen vibrational modes of the C=O· ·H—O—C moiety, which are at 1547 ($\nu_{C=O}$) and 1468 (ν_{C-O}) cm^{-1} respectively [20]. The IR spectrum of the 2-methyl derivative shows only a diketo doublet at 1687 and 1663 cm^{-1} for the out-of-phase and in-phase stretching of the two carbonyl groups. Other strong bands in the spectrum are at 1594, 1448, 1345, 1231, 1204, 968, 944 and 708 cm^{-1}. Some of these also show doublet character arising from the two C_6H_5CO fragments of the molecule.

The IR spectrum of the 2-(4-methoxyphenyl) compound is very similar with the two carbonyl peaks at 1697 and 1666 cm^{-1}. Other strong bands are observed at 1595, 1507, 1247, 801 and 690 cm^{-1}, again most having doublet structure.

Crystallography

Unit-cell parameters and intensity data were obtained by following previously detailed procedures [21] using a CAD 4 diffractometer operating in the ω—2θ scan mode, with Ni-filtered Cu K_α radiation (λ = 1.5418 Å). The reflection intensities for both structures were corrected for absorption, using the azimuthal-scan method [22]. The relevant experimental data are summarised in Table 2. The structures were solved by the application of direct methods (SHELX86) [23] and refined by full-matrix least-squares (SHELX76) [24]. The final cycles of refinement, for both structures, included all hydrogen atoms in their calculated positions (C—H = 0.96 Å, U = 0.10 Å^2). All non-hydrogen atoms were refined anisotropically.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 25 and 26 respectively.

All computations were made on a DEC VAX-11/750 computer. Atomic coordinates for $C_{16}H_{14}O_2$ and $C_{22}H_{18}O_3$ are given in Tables 3 and 4 respectively, and bond lengths and angles in Tables 5 and 6. Tables of isotropic hydrogen atom coordinates, anisotropic thermal coefficients and F_O/F_C values have been deposited as supplementary data*.

DISCUSSION

Clearly a β-diketone structure can be built into a molecule by having both protons on the α-carbon substituted by other groups. On the other hand the enol conformer can be the only possible arrangement if the α-carbon and one of the β-carbons are part of an aromatic ring, as in usnic acid for instance [27]. However when neither of these constraints applies then a variety of factors can determine the keto $\rightleftharpoons$ enol equilibrium position [28].

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*B.L.L.D. Supplementary Publication No. S.U.P. 26336 (45 pages).

TABLE 2

Crystal data, details of intensity measurements and structure refinement for 1,3-diphenyl-2-methylpropane-1,3-dione, $C_{16}H_{14}O_2$, and 1,3-diphenyl-2-(4-methoxyphenyl)-propane-1,3-dione, $C_{22}H_{18}O_3$

Formula	$C_{16}H_{14}O_2$	$C_{22}H_{18}O_3$
M	238.29	330.38
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$
a (Å)	10.301(1)	19.451(2)
b (Å)	9.980(1)	18.456(1)
c (Å)	12.685(1)	10.307(3)
β (°)	92.72(6)	105.05(1)
U (Å^3)	1302.7(2)	3573.0(12)
Z	4	8
D_c(g cm^{-3})	1.215	1.228
F(000)	504	1392
Crystal size (mm)	0.63 × 0.38 × 0.10	0.60 × 0.38 × 0.10
μ (cm^{-1})	5.96	6.14
Absorption corr. (min., max.) (%)	82, 100	81, 100
θ range	3.0, 70.0	3.0, 70.0
h, k, l range	$-12 \rightarrow 12, 0 \rightarrow 12, 0 \rightarrow 15$	$0 \rightarrow 23, 0 \rightarrow 22, -12 \rightarrow 12$
Intensity variations (%)	<3	<3
Total no. reflections	2748	7218
No. unique reflections	2469	6774
Significance test	$F_r > 3{,}0\sigma(F_O)$	$F_r > 3.0\sigma(F_O)$
No. reflections used in the refinement	1501	3106
No. refined parameters	167	458
Max. least-squares shift-to-error ratio	0.001	0.014
Min. and max. height in final difference Fourier map, $\Delta\rho/e$ (Å^{-3})	−0.19, 0.19	−0.09, 0.10
Function minimized	$\Sigma_w(\lvert F_O - \lvert F_C\rvert)^2$	$\Sigma_w(\lvert F_O\rvert - \lvert F_C\rvert)^2$
Weighting scheme parameter g in $w = 1/[\sigma^2(F_O) + gF_O^2]$	0.0004	0.0003
Final R	0.056	0.060
Final R_w	0.059	0.053

Not surprisingly, attention has focussed on the enol tautomer because of its strong hydrogen bond, which is often invoked as the reason why this conformer is most commonly observed. Table 1 lists eleven acyclic β-diketones whose molecular structures are known in the solid phase. All are enols. Some are surprisingly symmetrical as can be judged by the similarity in the carbon—oxygen bond lengths, one of which is formally a carbonly link, the other an alkoxy C—O bond. The intramolecular hydrogen bond within these systems is however non-centred in all cases [28].

TABLE 3

Fractional atomic coordinates (× 10^4) for 3-diphenyl-2-methylpropane-1,3-dione, $C_{16}H_{14}O_2$

Atom	Coordinate		
	x	*y*	*z*
O(1)	157(2)	2871(2)	9199(2)
O(2)	365(2)	1825(2)	6837(2)
C(1)	1126(3)	2973(3)	8682(2)
C(2)	1837(3)	1721(2)	8347(2)
C(3)	1393(3)	1376(3)	7212(2)
C(4)	2163(3)	423(3)	6605(2)
C(5)	1516(3)	−385(3)	5845(2)
C(6)	2181(4)	−1284(4)	5261(2)
C(7)	3511(4)	−1382(4)	5405(3)
C(8)	4173(3)	−597(3)	6133(3)
C(9)	3504(3)	304(3)	6752(2)
C(10)	1600(3)	4319(3)	8372(2)
C(11)	2665(3)	4491(3)	7775(3)
C(12)	3066(4)	5765(3)	7515(3)
C(13)	2424(4)	6865(3)	7861(3)
C(14)	1370(4)	6706(3)	8461(3)
C(15)	939(3)	5437(3)	8720(2)
C(16)	1540(4)	515(3)	9044(2)

Substitution at the 2 position of pentane-1,3-dione greatly affects the keto $\rightleftharpoons$ enol equilibrium, at least in solution, but in an unpredictable manner. Methyl substitution reduces the enol from 81% to 31%, whereas methylthio substitution increases it to 100%. A *p*-methoxyphenyl group produces a crystalline derivative whose IR spectrum suggests again that it is 100% enol [29]. This compound is being further examined.

Since phenyl and substituted phenyl derivatives are often solids these have attracted most attention as candidates for X-ray and neutron diffraction studies, as Table 1 shows. A few derivatives of pentane-2,4-dione are also solids, but the parent compound itself remained unanalysed until relatively recently when it turned up as a solvate molecule in a drug complex [11].

Substitution of a methyl or a *p*-methoxyphenyl group at the 2 position of DPP gave crystalline products, $C_{16}H_{14}O_2$ and $C_{22}H_{18}O_3$ respectively, that were suited to X-ray analysis and full structure determinations have been carried out. Both compounds exist as the diketo conformer in the solid phase, and both are the first examples of such molecules, shown in Figs. 1 and 2. Indeed we believe that the 2-methoxyphenyl derivative is the first example of its kind in which each carbon atom of a β-diketone carries an aromatic substituent.

Although both the methyl and methoxyphenyl substituents increase the steric congestion of the molecule and prevent the enol tautomers from

TABLE 4

Fractional atomic coordinates (× 10^4) for 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione, $C_{22}H_{18}O_3$

Atom	Coordinate		
	x	*y*	*z*
Molecule 1			
O(11)	9271(1)	2874(2)	3713(3)
O(12)	7707(1)	2949(2)	4282(3)
O(13)	9108(2)	6143(2)	2496(3)
C(11)	8709(2)	2692(2)	2964(4)
C(12)	8125(2)	3242(2)	2381(3)
C(13)	7547(2)	3177(2)	3130(4)
C(14)	6804(2)	3394(2)	2475(4)
C(15)	6296(2)	3322(2)	3199(4)
C(16)	5598(2)	3502(2)	2629(5)
C(17)	5397(2)	3753(2)	1340(5)
C(18)	5890(2)	3823(2)	602(4)
C(19)	6593(2)	3651(2)	1169(4)
C(110)	8574(2)	1913(2)	2587(4)
C(111)	9150(2)	1444(3)	2886(4)
C(112)	9074(3)	725(3)	2619(5)
C(113)	8415(3)	451(3)	2024(5)
C(114)	7836(3)	911(3)	1683(5)
C(115)	7913(2)	1637(2)	1969(4)
C(116)	8396(2)	4014(2)	2463(4)
C(117)	8673(2)	4358(2)	3669(4)
C(118)	8931(2)	5068(2)	3729(4)
C(119)	8899(2)	5436(2)	2565(4)
C(120)	8620(2)	5103(2)	1347(4)
C(121)	8376(2)	4395(2)	1289(4)
C(122)	9434(3)	6500(3)	3715(5)
Molecule 2			
O(21)	560(1)	7293(1)	1548(3)
O(22)	2128(1)	7270(1)	687(3)
O(23)	1036(2)	10574(2)	2561(3)
C(21)	1147(2)	7072(2)	2113(4)
C(22)	1768(2)	7595(2)	2641(3)
C(23)	2315(2)	7501(2)	1836(4)
C(24)	3073(2)	7711(2)	2432(4)
C(25)	3538(2)	7700(2)	1614(4)
C(26)	4245(2)	7871(2)	2146(5)
C(27)	4498(2)	8054(2)	3477(4)
C(28)	4042(2)	8068(2)	4295(4)
C(29)	3326(2)	7905(2)	3769(4)
C(210)	1279(2)	6279(2)	2334(4)
C(211)	714(2)	5806(2)	1909(4)
C(212)	805(3)	5073(2)	2088(5)
C(213)	1462(3)	4796(2)	2701(5)
C(214)	2025(2)	5258(2)	3145(4)
C(215)	1940(2)	5992(2)	2964(4)
C(216)	1549(2)	8388(2)	2578(4)
C(217)	1286(2)	8736(2)	1371(4)
C(218)	1102(2)	9469(2)	1321(4)
C(219)	1188(2)	9847(2)	2491(5)
C(220)	1451(2)	9512(2)	3715(4)
C(221)	1625(2)	8781(2)	3748(4)
C(222)	814(3)	10957(2)	1350(5)

TABLE 5

Bond lengths (Å) and bond angles (°) for 1,3-diphenyl-2-methylpropane-1,3-dione, $C_{16}H_{14}O_2$

Bond	Length	Angle	Value
C(1)—O(1)	1.223(4)	C(2)—C(1)—O(1)	119.9(4)
C(2)—C(1)	1.519(5)	C(10)—C(1)—C(2)	120.0(3)
C(3)—C(2)	1.529(6)	C(16)—C(2)—C(1)	111.9(3)
C(4)—C(3)	1.478(5)	C(2)—C(3)—O(2)	119.8(3)
C(9)—C(4)	1.391(5)	C(4)—C(3)—C(2)	119.5(3)
C(7)—C(6)	1.378(5)	C(9)—C(4)—C(3)	122.6(3)
C(9)—C(8)	1.397(5)	C(6)—C(5)—C(4)	121.1(4)
C(15)—C(10)	1.391(5)	C(8)—C(7)—C(6)	120.6(4)
C(13)—C(12)	1.365(5)	C(8)—C(9)—C(4)	119.5(4)
C(15)—C(14)	1.386(5)	C(15)—C(10)—C(1)	117.9(3)
C(3)—O(2)	1.225(4)	C(12)—C(11)—C(10)	120.2(4)
C(10)—C(1)	1.489(5)	C(14)—C(13)—C(12)	119.7(4)
C(16)—C(2)	1.532(6)	C(14)—C(15)—C(10)	119.4(4)
C(5)—C(4)	1.400(5)	C(10)—C(1)—O(1)	120.2(3)
C(6)—C(5)	1.367(5)	C(3)—C(2)—C(1)	108.8(3)
C(8)—C(7)	1.368(5)	C(16)—C(2)—C(3)	107.9(3)
C(11)—C(10)	1.373(5)	C(4)—C(3)—O(2)	120.6(3)
C(12)—C(11)	1.381(5)	C(5)—C(4)—C(3)	118.7(3)
C(14)—C(13)	1.365(5)	C(9)—C(4)—C(5)	118.7(4)
		C(7)—C(6)—C(5)	119.7(4)
		C(9)—C(8)—C(7)	120.3(4)
		C(11)—C(10)—C(1)	122.7(3)
		C(15)—C(10)—C(11)	119.4(4)
		C(13)—C(12)—C(11)	120.6(4)
		C(15)—C(14)—C(13)	120.7(4)

forming, the two oxygens of the carbonyl groups remain in the *cis* configuration with dihedral angles close to that calculated by ab initio methods [16].

The C=O bond lengths in our derivatives are 1.223(4) and 1.225(4) Å for $C_{16}H_{14}O_2$ and 1.211(5), 1.221(5), 1.210(5) and 1.222(5) Å in the two molecules of $C_{22}H_{18}O_3$. These are all shorter than the values in Table 1, where the distinction between the C=O and C—O bonds is blurred in nearly all cases.

The O· · O distances of 3.189(3) Å (2-methyl) and 3.248(4) Å and 3.393(4) Å (for the two molecules of the 2-(4-methoxyphenyl) compound) are larger than the sum of the van der Waals radii for oxygen (1.50 Å) [30] and significantly larger than O· · O distances found for enol analogues such as DPP itself (2.460 Å) [6].

Since the ^1H NMR spectra also show both of the β-diketones to be 100% keto it is clear that the diketo configuration is not an artefact of the solid state. Substitution of the 2 position of DPP puts added steric strain on the molecule which the OHO hydrogen bond is powerless to overcome despite its strength. The molecules relax to the Z, Z diketone configuration with

TABLE 6

Bond lengths (Å) and bond angles (°) for 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione, $C_{22}H_{18}O_3$

Bond	Length	Bond	Length
Molecule 1			
C(11)—O(11)	1.211(5)	C(13)—O(12)	1.221(5)
C(119)—O(13)	1.375(5)	C(122)—O(13)	1.415(5)
C(12)—C(11)	1.526(7)	C(110)—C(11)	1.494(6)
C(13)—C(12)	1.525(6)	C(116)—C(12)	1.514(6)
C(14)—C(13)	1.483(5)	C(15)—C(14)	1.390(6)
C(19)—C(14)	1.385(5)	C(16)—C(15)	1.373(6)
C(17)—C(16)	1.364(6)	C(18)—C(17)	1.376(6)
C(19)—C(18)	1.378(6)	C(111)—C(110)	1.386(6)
C(115)—C(110)	1.375(6)	C(112)—C(111)	1.355(7)
C(113)—C(112)	1.366(7)	C(114)—C(113)	1.381(7)
C(115)—C(114)	1.372(6)	C(117)—C(116)	1.376(5)
C(121)—C(116)	1.392(6)	C(118)—C(117)	1.398(6)
C(119)—C(118)	1.366(6)	C(120)—C(119)	1.376(6)
C(121)—C(120)	1.386(6)		
Molecule 2			
C(21)—O(21)	1.210(5)	C(23)—O(22)	1.222(5)
C(219)—O(23)	1.381(5)	C(222)—O(23)	1.401(5)
C(22)—C(21)	1.532(6)	C(210)—C(21)	1.494(6)
C(23)—C(22)	1.520(7)	C(216)—C(22)	1.520(6)
C(24)—C(23)	1.493(5)	C(25)—C(24)	1.389(5)
C(29)—C(24)	1.385(5)	C(26)—C(25)	1.379(6)
C(27)—C(26)	1.374(6)	C(28)—C(27)	1.374(6)
C(29)—C(28)	1.390(5)	C(211)—C(210)	1.381(5)
C(215)—C(210)	1.387(6)	C(212)—C(211)	1.371(6)
C(213)—C(212)	1.369(6)	C(214)—C(213)	1.369(6)
C(215)—C(214)	1.371(6)	C(217)—C(216)	1.376(5)
C(221)—C(216)	1.382(5)	C(218)—C(217)	1.398(6)
C(219)—C(218)	1.365(6)	C(220)—C(219)	1.378(6)
C(221)—C(220)	1.389(6)		

Angle	Value	Angle	Value
Molecule 1			
C(122)—O(13)—C(119)	117.8(4)	C(12)—C(11)—O(11)	121.6(5)
C(110)—C(11)—O(11)	120.1(5)	C(110)—C(11)—C(12)	118.3(4)
C(13)—C(12)—C(11)	108.6(4)	C(116)—C(12)—C(11)	113.0(4)
C(116)—C(12)—C(13)	109.7(4)	C(12)—C(13)—O(12)	119.0(4)
C(14)—C(13)—O(12)	120.6(4)	C(14)—C(13)—C(12)	120.5(4)
C(15)—C(14)—C(13)	118.2(4)	C(19)—C(14)—C(13)	122.9(4)
C(19)—C(14)—C(15)	118.9(4)	C(16)—C(15)—C(14)	120.5(5)
C(17)—C(16)—C(15)	120.1(5)	C(18)—C(17)—C(16)	120.3(5)
C(19)—C(18)—C(17)	120.2(5)	C(18)—C(19)—C(14)	120.1(5)
C(111)—C(110)—C(11)	117.7(5)	C(115)—C(110)—C(11)	123.9(5)
C(115)—C(110)—C(111)	118.4(5)	C(112)—C(111)—C(110)	121.9(5)
C(113)—C(112)—C(111)	119.6(6)	C(114)—C(113)—C(112)	119.6(6)

TABLE 6 (continued)

Angle	Value	Angle	Value
C(115)–C(114)–C(113)	120.6(5)	C(114)–C(115)–C(110)	119.9(5)
C(117)–C(116)–C(12)	122.3(4)	C(121)–C(116)–C(12)	119.8(4)
C(121)–C(116)–C(117)	117.9(5)	C(118)–C(117)–C(116)	121.7(5)
C(119)–C(118)–C(117)	119.5(5)	C(118)–C(119)–O(13)	124.8(5)
C(120)–C(119)–O(13)	115.4(5)	C(120)–C(119)–C(118)	119.8(5)
C(121)–C(120)–C(119)	120.7(5)	C(120)–C(121)–C(116)	120.5(5)
Molecule 2			
C(222)–O(23)–C(219)	117.7(4)	C(22)–C(21)–O(21)	121.2(4)
C(210)–C(21)–O(21)	120.4(4)	C(210)–C(21)–C(22)	118.3(4)
C(23)–C(22)–C(21)	109.5(4)	C(216)–C(22)–C(21)	113.8(4)
C(216)–C(22)–C(23)	108.4(4)	C(22)–C(23)–O(22)	119.7(4)
C(24)–C(23)–O(22)	120.2(4)	C(24)–C(23)–C(22)	120.1(4)
C(25)–C(24)–C(23)	118.4(4)	C(29)–C(24)–C(23)	122.3(4)
C(29)–C(24)–C(25)	119.3(4)	C(26)–C(25)–C(24)	119.7(5)
C(27)–C(26)–C(25)	121.0(5)	C(28)–C(27)–C(26)	119.8(5)
C(29)–C(28)–C(27)	119.9(5)	C(28)–C(29)–C(24)	120.3(5)
C(211)–C(210)–C(21)	118.7(4)	C(215)–C(210)–C(21)	123.1(4)
C(215)–C(210)–C(211)	118.2(5)	C(212)–C(211)–C(210)	121.1(5)
C(213)–C(212)–C(211)	120.2(5)	C(214)–C(213)–C(212)	119.4(5)
C(215)–C(214)–C(213)	120.8(5)	C(214)–C(215)–C(210)	120.3(5)
C(217)–C(216)–C(22)	121.5(4)	C(221)–C(216)–C(22)	120.2(4)
C(221)–C(216)–C(217)	118.3(5)	C(218)–C(217)–C(216)	121.2(5)
C(219)–C(218)–C(217)	119.3(5)	C(218)–C(219)–O(23)	124.3(5)
C(220)–C(219)–O(23)	114.9(5)	C(220)–C(219)–C(218)	120.8(5)
C(221)–C(220)–C(219)	119.2(5)	C(220)–C(221)–C(216)	121.3(5)

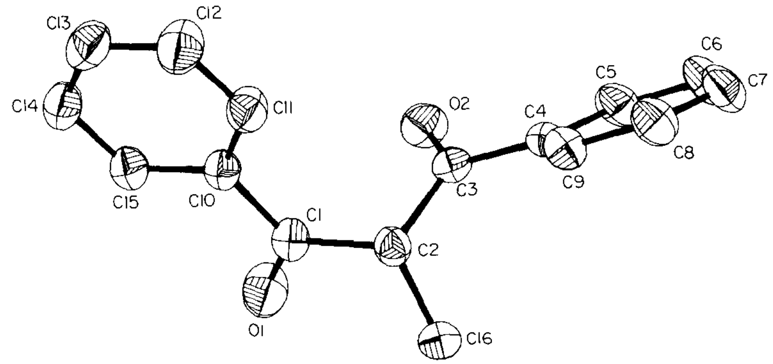

Fig. 1. Structure and atom labelling of 1,3-diphenyl-2-methylpropane-1,3-dione, protons omitted.

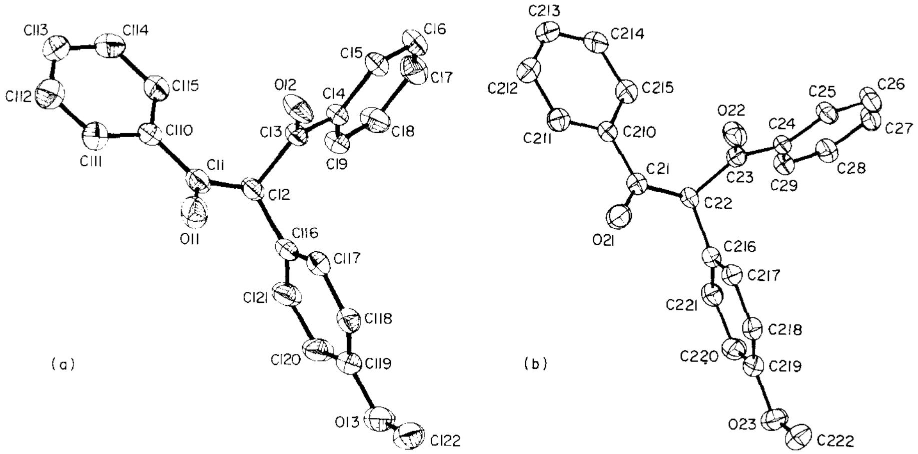

Fig. 2. Structure and atom labelling of 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione, protons omitted.

dihedral angles about that predicted, although as the two molecules of the 2-(4-methoxyphenyl) derivative show, the value of the angle is probably determined by lattice forces.

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