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Structure of 3,4-Dihydroxy-1,6-diphenyl-2,4-hexadiene-1,6-dione (I) and its 1,6-Di-*p*-tolyl Analogue (II)

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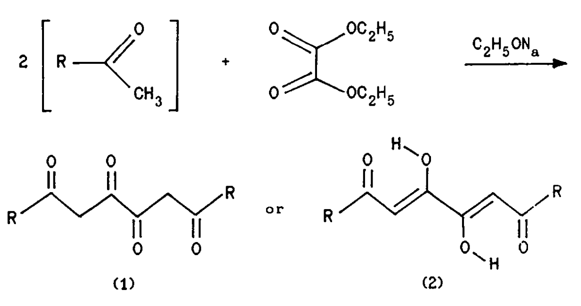
Abstract. (I) $C_{18}H_{14}O_4$, $M_r = 294{\cdot}31$, monoclinic, $P2_1/n$, $a = 15{\cdot}351\,(2)$, $b = 9{\cdot}074(1)$, $c = 5{\cdot}196\,(1)$ Å, $\beta = 97{\cdot}84\,(1)^\circ$, $V = 717{\cdot}0\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}36$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}900$ cm^{-1}, $F(000) = 308$, $T = 293$ K, $R = 0{\cdot}060$ for 504 observed independent reflections with $F_o \geq 3\sigma(F_o)$. (II) $C_{20}H_{18}O_4$, $M_r = 322{\cdot}36$, monoclinic, $P2_1/c$, $a = 15{\cdot}048\,(3)$, $b = 6{\cdot}179\,(1)$, $c = 8{\cdot}685\,(2)$ Å, $\beta = 92{\cdot}55\,(2)^\circ$, $V = 806{\cdot}8\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}32$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}859$ cm^{-1}, $F(000) = 340$, $T = 293$ K, $R = 0{\cdot}042$, $wR = 0{\cdot}043$ for 922 unique reflections with $F_o \geq 3\sigma(F_o)$. Both structures consist of individual centrosymmetric molecules occupying special positions 2(*a*) (I) and 2(*c*) (II). The molecules are linked together by van der Waals interactions. An intramolecular O—H···O hydrogen bond is present in both (I) and (II) with O1···O2 distances of 2·487 (8) and 2·539 (2) Å, respectively.

Introduction. On treating either acetophenone or *p*-methylacetophenone with diethyl oxalate, stable crystalline substances (I) and (II) are formed; because of keto–enol tautomerism, structures (1) and (2) are possible. Since it was not possible to establish the structure by IR spectroscopy an X-ray structural analysis was undertaken.



(I) $R = C_6H_5$—
(II) $R = CH_3C_6H_5$—

Experimental. The title compounds were prepared in one step by condensation of acetophenone or *p*-methylacetophenone with diethyl oxalate in the presence of sodium ethoxide (Claisen & Stylos, 1888). Yellow needle-shaped (I) and yellow prismatic (II) crystals were recrystallized from chloroform. Lattice parameters for (I) and (II) were determined by a least-squares fit of 16 (I) and 20 (II) reflections measured on a Philips PW1100 diffractometer in the range $5 < \theta < 15^\circ$; monochromatized Mo $K\alpha$ radiation; θ–2θ scan mode; scan speed 0·04° s^{-1}; scan width 1·20°; three standard reflections measured every 2 h showed only random fluctuations; θ range 2–27°; data reduction by a local program; an absorption correction was not applied. The structures were solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by a standard full-matrix least-squares method (Rizzoli, Sangermano, Calestani & Andreetti, 1987). Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from geometrical considerations or in subsequent difference Fourier maps. They were included in structure-factor calculations with an overall isotropic thermal parameter but were not refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149–150). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1$ for (I) and $w = 1/(\sigma^2 F_o)$ for (II).

(I) Crystal size 0·10 × 0·10 × 0·40 mm; $-18 < h < 18$, $0 < k < 10$, $0 < l < 6$; 664 reflections collected; 581 unique reflections; 504 with $F_o \geq 3\sigma(F_o)$; $R_{\text{int}} = 0{\cdot}030$; for the hydrogen atoms $U_{\text{iso}} = 0{\cdot}117$ Å^2; $R = 0{\cdot}060$; 101 parameters refined; $(\Delta/\sigma)_{\max} = 0{\cdot}018$; $S = 1{\cdot}0013$; $-0{\cdot}21 < \Delta\rho < 0{\cdot}23$ e Å^{-3}.

(II) Crystal dimensions 0·20 × 0·30 × 0·40 mm; $-20 < h < 20$, $0 < k < 8$, $0 < l < 12$; 1157 reflections collected; 1095 unique reflections; 922 with $F_o \geq 3\sigma(F_o)$; $R_{\text{int}} = 0{\cdot}053$; for the hydrogen atoms $U_{\text{iso}} =$

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Table 1. *Final atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* [Å^2 × 10^3 *for* (I), Å^2 × 10^4 *for* (II)] *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(I)				
O1	−831 (3)	1291 (6)	405 (11)	72 (2)
O2	−319 (3)	2865 (6)	4231 (11)	71 (2)
C1	−64 (5)	613 (9)	920 (14)	52 (3)
C2	552 (4)	992 (9)	2907 (14)	49 (3)
C3	404 (5)	2179 (9)	4609 (15)	52 (3)
C4	1053 (4)	2657 (9)	6790 (14)	48 (3)
C5	873 (5)	3874 (9)	8243 (16)	64 (3)
C6	1452 (6)	4310 (10)	10381 (17)	76 (4)
C7	2231 (6)	3566 (11)	11075 (19)	77 (4)
C8	2425 (5)	2378 (11)	9621 (17)	74 (3)
C9	1850 (5)	1911 (9)	7475 (15)	60 (3)
(II)				
O1	75 (1)	2819 (2)	5233 (2)	497 (6)
O2	1288 (1)	3627 (2)	7278 (2)	485 (6)
C1	266 (1)	762 (3)	5484 (2)	372 (7)
C2	905 (2)	89 (3)	6541 (3)	415 (8)
C3	1416 (1)	1620 (4)	7440 (2)	405 (8)
C4	2124 (1)	881 (4)	8568 (2)	402 (8)
C5	2762 (1)	2359 (4)	9103 (3)	499 (8)
C6	3434 (2)	1749 (4)	10149 (3)	571 (9)
C7	3482 (2)	−354 (5)	10703 (3)	513 (9)
C8	2837 (2)	−1818 (4)	10194 (3)	519 (8)
C9	2172 (2)	−1221 (4)	9121 (3)	474 (8)
C10	4214 (2)	−1053 (5)	11844 (3)	740 (12)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *involving non*-H *atoms*

	(I)	(II)
O1—C1	1·323 (9)	1·319 (2)
O2—C3	1·264 (9)	1·262 (3)
C1—C1^i	1·497 (11)	1·475 (2)
C1—C2	1·346 (9)	1·364 (3)
C2—C3	1·431 (11)	1·429 (3)
C3—C4	1·469 (10)	1·487 (2)
C4—C5	1·387 (11)	1·390 (3)
C4—C9	1·401 (10)	1·385 (3)
C5—C6	1·382 (11)	1·381 (3)
C6—C7	1·378 (13)	1·386 (4)
C7—C8	1·372 (14)	1·385 (4)
C8—C9	1·390 (11)	1·387 (4)
C7—C10	–	1·511 (4)
O1—C1—C2	123·3 (7)	123·1 (2)
O1—C1—C1^i	114·0 (6)	114·3 (2)
C1^i—C1—C2	122·7 (7)	122·5 (2)
C1—C2—C3	120·8 (7)	120·8 (2)
O2—C3—C2	119·0 (7)	120·9 (2)
C2—C3—C4	123·4 (7)	120·6 (2)
O2—C3—C4	117·6 (7)	118·5 (2)
C3—C4—C9	122·0 (7)	122·8 (2)
C3—C4—C5	119·4 (6)	118·8 (2)
C5—C4—C9	118·6 (7)	118·4 (2)
C4—C5—C6	120·8 (7)	121·0 (2)
C5—C6—C7	120·7 (8)	120·6 (3)
C6—C7—C8	119·1 (8)	118·5 (3)
C7—C8—C9	121·3 (8)	121·0 (2)
C4—C9—C8	119·6 (8)	120·5 (2)
C6—C7—C10	–	121·4 (3)
C8—C7—C10	–	120·2 (3)

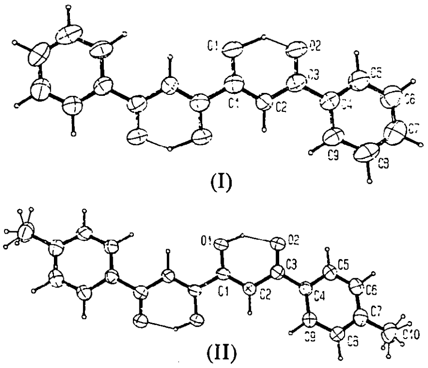
Symmetry code: (i) $-x$, $-y$, $-z$ (I); $-x$, $-y$, $-z+1$ (II).

0·070 and 0·091 Å^2 for the disordered methyl hydrogens; R = 0·042; wR = 0·043; 111 parameters refined; $(\Delta/\sigma)_{max}$ = 0·008 in the last cycle; −0·20 < $\Delta\rho$ < 0·14 e Å^{-3}. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2.*

Discussion. Drawings of molecules (I) and (II) with their numbering schemes are shown in Fig. 1. The shortest intermolecular contact in (I) is O2···C5^i [(i) = $-x$, $-y+1$, $-z+1$] 3·29 (1) Å; however, in (II) there is one short oxygen-to-oxygen contact O1···O1^i [(i) = $-x$, $-y+1$, $-z+1$] 2·733 (2) Å which is not a hydrogen bond because the hydrogen atom belonging to O1, in (II), participates in an intramolecular hydrogen bond. The bond distances and bond angles lie within normal ranges and display a close correspondence between equivalents in the two different molecules. The methyl groups in (II) are disordered.

The unsaturated chain connecting the benzene rings is planar within standard deviations [maximum deviation 0·004 (8) Å for C3 in (I) and 0·011 (3) Å for C2 in (II)]. The structural study unequivocally showed that the compounds are in the enol form (2) (see Table 2). The position of the hydrogen atoms included in intramolecular hydrogen bonding was determined as an electron density of 0·35 in (I) and 0·26 e Å^{-3} in (II). While the hydrogen atom is almost at the same distance to the O1 and O2 atoms in (I) (1·311 and 1·358 Å, respectively), the hydrogen is clearly bonded to O1 in (II) (O1—H···O2; O1—H 1·030 and H···O2 1·640 Å).

Methyl substitution may be responsible for differences in molecular packing and for the rotation



(I)

(II)

Fig. 1. *ORTEP*II (Johnson, 1976) plots of the molecules (I) and (II) showing the numbering schemes. Thermal ellipsoids at the 50% probability level. Hydrogen atoms are represented by circles or arbitrary radius. The disordered methyl groups are shown.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54369 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the benzene ring around the C3—C4 single bond. The angle between least-squares planes calculated through the unsaturated chain and benzene ring is 3·96 (19) in (I) and 17·94 (7)° in (II).

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Structure of 2,3-Diphenacylquinoxaline

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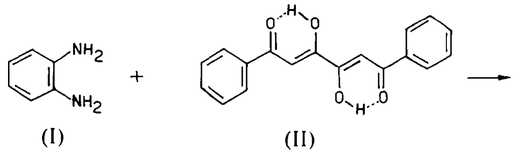
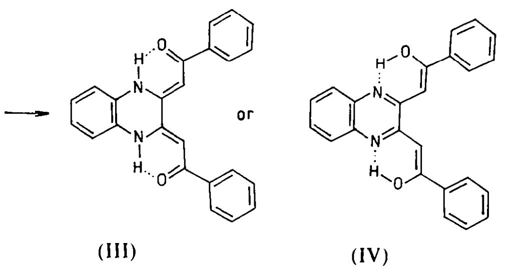
Abstract. $C_{24}H_{18}N_2O_2$, $M_r = 366{\cdot}42$, orthorhombic, $Pbcn$, $a = 23{\cdot}254\,(6)$, $b = 11{\cdot}495\,(3)$, $c = 6{\cdot}944\,(2)$ Å, $V = 1856{\cdot}2\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 6{\cdot}356$ cm^{-1}, $F(000) = 768$, $T = 293$ K, $R = 0{\cdot}048$, $wR = 0{\cdot}056$ for 1042 unique reflections with $I \geq 2\sigma(I)$. The structure is built up of discrete molecules held together by van der Waals interactions only. The molecule is placed in the special position 4(*c*) possessing crystallographic C_2 symmetry. An intramolecular N—H···O hydrogen bond is present in the structure.

Introduction. The 3,4-dihydroxy-1,6-diphenyl-2,4-hexadiene-1,6-dione (II) is a product of the reaction between acetophenone and diethyl oxalate (Kaitner, Jovanovski & Janev, 1992). This substance reacts with *o*-phenylenediamine (I) and the resulting product is 2,3-diphenacylquinoxaline. It was not possible to distinguish between tautomers (III) and (IV) by infrared spectroscopy. An X-ray structure determination was therefore undertaken.



(I) (II)



(III) (IV)

Experimental. The title compound was obtained upon mixing and refluxing ethanol solutions of *o*-phenylenediamine and 3,4-dihydroxy-1,6-diphenyl-2,4-hexadiene-1,6-dione in an equimolar ratio. The microcrystalline product was recrystallized from ethanol; red–orange needle-shaped crystals were used in the structure determination.

Accurate cell dimensions and the crystal orientation matrix were determined on a Philips PW1100 automatic four-circle diffractometer by a least-squares treatment of the setting angles of 16 reflections in the range $7 < \theta < 15°$. Crystal dimensions were $0{\cdot}15 \times 0{\cdot}16 \times 0{\cdot}30$ mm. The intensities of reflections h 0 to 29, k 0 to 15, l 0 to 9 with $2 < \theta < 70°$ were measured using the θ–2θ scan mode; scan width 1·0°; scan speed 0·04° s^{-1}; graphite-monochromatized Cu $K\alpha$ radiation. Intensities of

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