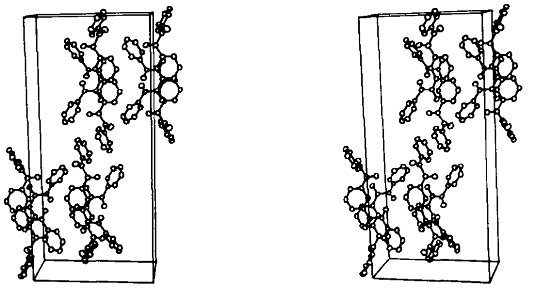

Fig. 2. Stereoview of the molecular packing in the unit cell.

Three of the four carbonyl groups show small but significant deviations from planarity. The largest deviations are observed in the C(7)C(8)O(1)C(9) group, where C(8) is 0·043 (2) Å from the least-squares plane through the four atoms. In contrast, the C(15)-C(16)O(4)C(17) is highly planar, with C(16) only 0·003 (3) Å from the least-squares plane. The C(16)—C(17) distance [1·460 (4) Å] is shorter than the C(8)—C(9) distance [1·476 (4) Å], possibly indicating greater conjugation of the O(4)—C(16) bond with the phenyl ring, in agreement with the much smaller torsion angle O(4)C(16)C(17)C(18) [−0·5°] compared with O(1)C(8)C(9)C(10) [−19·4°].

The average C—O distance, 1·24 Å, agrees well with various carbonyl bond lengths observed in other similar compounds (Brown & Colclough, 1983; Hirshfeld & Rabinovich, 1967; Fonseca, Martínez-Carrera & García-Blanco, 1982). The C(7)—C(8) and C(15)—C(16) distances, 1·524 (4) and 1·535 (4) Å, are very close to a C($sp^3$)—C($sp^3$) bond (1·54 Å) (Greenhough & Trotter, 1980; Acton, Roth, Katz, Frank, Maier & Paul, 1972), while C(1)—C(7) [1·483 (4) Å], C(8)—C(9) [1·476 (4) Å], C(3)—C(15) [1·475 (4) Å] and C(16)—C(17) [1·460 (4) Å] are similar and correspond to the C($sp^2$)—C($sp^2$) distances (1·48 Å) (Somayajulu, 1959; Kuchitsu, Fukuyama & Morino, 1968). The stereoscopic view of the molecular packing is shown in Fig. 2. The molecules are held together by van der Wäals forces. No unusually short intermolecular distances were noticed.

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# The Structure of 2,2′-Diphenyl-1,1′-(1,4-phenylene)diethanedione, $C_{22}H_{14}O_4$

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(*Received* 5 *July* 1983; *accepted* 14 *March* 1984)

**Abstract.** $M_r = 342{\cdot}4$, triclinic, $P\bar{1}$, $a = 4{\cdot}466\,(2)$, $b = 12{\cdot}785\,(2)$, $c = 16{\cdot}104\,(2)$ Å, $\alpha = 68{\cdot}46\,(1)$, $\beta = 88{\cdot}16\,(2)$, $\gamma = 88{\cdot}08\,(2)°$, $V = 854{\cdot}67\,(14)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}330$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}9$ cm$^{-1}$, $F(000) = 356$, $T = 300$ K, final $R = 0{\cdot}035$, $R_w = 0{\cdot}047$ for 1555 independent reflections. The molecular structure is closely related to that of 2,2′-diphenyl-1,1′-(1,3-phenylene)diethanedione with twisted

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* On leave from Tata Iron & Steel Co., Jamshedpur, India.

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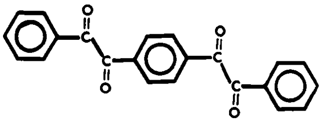
phenyl rings. The asymmetric unit, however, consists of two half-molecules at different centers of symmetry. Carbonyl groups are arranged in an antiparallel configuration and molecular packing is determined by van der Waals interactions.

**Introduction.** The crystal structure analysis of the title compound, $C_{22}H_{14}O_4$, was undertaken as a continuation of a program to determine the structures of benzophenones and related compounds to study the changes between ground- and excited-state geometry of the carbonyl group. The crystal structure of 2,2′-diphenyl-1,1′-(1,3-phenylene)diethanedione has been determined previously (Syed, Stevens & Klein, 1984). The present results also allow a comparative study of the two similar systems.



**Experimental.** Yellow crystals, obtained with difficulty, by evaporating a solution of the title compound in mixture of acetone–cyclohexene in equal amounts. Data collected on Enraf–Nonius CAD-4 diffractometer from crystal 0·12 × 0·12 × 0·48 mm; graphite-monochromated Mo $K\alpha$; cell constants from least-squares analysis of 25 reflections with $16 \leq 2\theta \leq 30°$ measured on diffractometer; lack of systematic absences and cell dimensions indicated triclinic space group with $Z = 2$, successful determination of structure confirmed space group $P\bar{1}$; intensity data collected in $\omega$:$2\theta$ scan mode; 5065 independent reflections, $2\theta \leq 60°$; $-6 \leq h \leq 6$, $0 \leq k \leq 18$, $-22 \leq l \leq 22$; 1555 treated as observed [$I > 3\sigma(I)$, where $\sigma(I)$ is e.s.d. based on counting statistics] and used in least squares; 3 intensity standards measured every 2 h showed no significant variations in intensities; Lorentz–polarization correction, no absorption correction; overall temperature ($B = 5{\cdot}17$ Å$^2$) and scale factors determined and used to compute normalized structure amplitudes; structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978; Frenz, 1982) based on 334 reflections, $4{\cdot}80 \leq E \leq 1{\cdot}74$. All non-hydrogen atoms located in $E$ map. Isotropic refinement, full-matrix least squares, unit weights, $R = 0{\cdot}10$ for non-H atoms; 14 H atoms placed at calculated positions (C—H = 0·95 Å), further refinement, full-matrix least squares, anisotropic for non-H atoms and fixed individual isotropic temperature factors for H(3), H(4), H(5), H(20), H(21) and H(22). Final cycle of refinement, isotropic temperature factors for H's, anisotropic for non-H's, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, converged at $R = 0{\cdot}035$, $R_w = 0{\cdot}047$; largest parameter $\Delta/\sigma = 0{\cdot}01$; extinction correction applied in final cycles refined to a coefficient = $3{\cdot}13 \times 10^{-7}$ mm. No significantly large positive or negative electron-density peaks in final difference-Fourier synthesis; largest positive region 0·09 e Å$^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on PDP 11/34 computer using the *SDP* program system (Frenz, 1982).*

**Discussion.** Final atomic coordinates and equivalent isotropic temperature factors together with their e.s.d.'s in parentheses are listed in Table 1. Bond distances and angles are given in Table 2. The numbering scheme and conformation of the molecule are shown in the *ORTEP* (Johnson, 1976) plot in Fig. 1. The molecular symmetry coincides with that of the unit cell.

Within experimental error, the geometrical parameters of the phenyl rings C(1)C(2)C(3)C(4)-C(5)C(6), C(18)C(19)C(20)C(21)C(22)C(23), C(9)-C(10)C(14)C(9′)C(10′)C(14′) and C(11)C(12)C(13)-C(11′)C(12′)C(13′), hereafter called I, II, III and IV, are normal and consistent with those obtained for 2,2′-diphenyl-1,1′-(1,3-phenylene)diethanedione (Syed, Stevens & Klein, 1984). However, the deviations from planarity of O(2) [−0·457 (2) Å] and O(3) [−1·438 (2) Å] with respect to III and IV, respectively, are larger but agree well with the twisted geometry of similar compounds (van der Heijdin, Griffith, Chandler & Robertson, 1975). The observed dihedral angles between I and III [101·7 (3)°] and II and IV [136·3 (3)°], together with the antiparallel arrangement of C=O groups, allow the molecule to adopt the stable stereochemical conformation of this and similar molecules (Syed, Stevens & Klein, 1984). Table 3 lists the torsion angles of interest which indicate the molecular conformation as a whole. In contrast to 2,2′-diphenyl-1,1′-(1,3-phenylene)diethanedione, the carbonyl groups show smaller deviations from planarity. The largest deviation is observed in the C(7)C(8)-O(2)C(9) group where C(8) is 0·027 (3) Å from a least-squares plane through the four atoms.

The average distance for the C=O bond, 1·217 (3) Å, agrees well with the value of 1·215 (5) Å as proposed by Sutton (1965) and with 1·214 Å found in 2,2′-diphenyl-1,1′-(1,3-phenylene)diethanedione (Syed, Stevens & Klein, 1984, and references therein). The C(7)—C(8) and C(16)—C(17) distances are in accord with the C($sp^3$)—C($sp^3$) bond reported for similar systems (Bonham, Bartell & Kohl, 1959; Greenhough & Trotter, 1980; Acton, Roth, Katz, Frank, Maier & Paul, 1972; Syed, Stevens & Klein, 1984), while other C—C distances, which average 1·475 Å, correspond to typical C($sp^2$)—C($sp^2$) bonds, 1·48 Å (Somayajulu,

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* Lists of structure factors, additional bond distances and angles and anisotropic thermal parameters have been deposited with British Library Lending Division as Supplementary Publication No. SUP 39344 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:

$\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\cos(\gamma)\beta_{12} + ac\cos(\beta)\beta_{13} + bc\cos(\alpha)\beta_{23}]$.

| | $x$ | $y$ | $z$ | $B$ or $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·5797 (5) | 0·2240 (2) | 0·1843 (1) | 7·88 (6) |
| O(2) | 0·6233 (6) | 0·2616 (2) | −0·0217 (1) | 8·54 (6) |
| O(3) | 0·0527 (5) | 0·2201 (2) | 0·3357 (1) | 8·12 (6) |
| O(4) | 0·0616 (5) | 0·2954 (2) | 0·5027 (1) | 8·03 (6) |
| C(1) | 0·8837 (6) | 0·0874 (2) | 0·1517 (2) | 5·09 (6) |
| C(2) | 1·0675 (7) | 0·0627 (2) | 0·0904 (2) | 6·10 (7) |
| C(3) | 1·1993 (7) | −0·0423 (2) | 0·1128 (2) | 7·55 (9) |
| C(4) | 1·1518 (8) | −0·1221 (2) | 0·1950 (2) | 8·13 (9) |
| C(5) | 0·9774 (8) | −0·0985 (3) | 0·2570 (2) | 7·84 (9) |
| C(6) | 0·8425 (7) | 0·0060 (2) | 0·2361 (2) | 6·61 (8) |
| C(7) | 0·7322 (6) | 0·1979 (2) | 0·1308 (2) | 5·75 (7) |
| C(8) | 0·7444 (7) | 0·2852 (2) | 0·0356 (2) | 6·06 (7) |
| C(9) | 0·8764 (6) | 0·3958 (2) | 0·0185 (1) | 4·92 (6) |
| C(10) | 0·8342 (6) | 0·4817 (2) | −0·0633 (2) | 5·65 (7) |
| C(11) | 0·5291 (6) | 0·0912 (2) | 0·5255 (2) | 5·73 (7) |
| C(12) | 0·3546 (6) | 0·1018 (2) | 0·4533 (1) | 5·02 (6) |
| C(13) | 0·3272 (6) | 0·0092 (2) | 0·4288 (2) | 5·81 (7) |
| C(14) | 1·0441 (6) | 0·4152 (2) | 0·0817 (2) | 5·55 (7) |
| C(16) | 0·1965 (7) | 0·2087 (2) | 0·4015 (2) | 5·90 (7) |
| C(17) | 0·1985 (7) | 0·3075 (2) | 0·4331 (2) | 5·87 (7) |
| C(18) | 0·3476 (6) | 0·4115 (2) | 0·3782 (1) | 4·99 (6) |
| C(19) | 0·5157 (6) | 0·4192 (2) | 0·3026 (2) | 5·93 (7) |
| C(20) | 0·6570 (7) | 0·5169 (3) | 0·2544 (2) | 7·04 (8) |
| C(21) | 0·6334 (8) | 0·6065 (3) | 0·2811 (2) | 7·67 (9) |
| C(22) | 0·4709 (8) | 0·6003 (2) | 0·3554 (2) | 7·49 (9) |
| C(23) | 0·3297 (7) | 0·5034 (2) | 0·4041 (2) | 6·35 (8) |
| H(10) | 0·712 (5) | 0·467 (2) | −0·104 (1) | 5·9 (5)* |
| H(14) | 1·065 (5) | 0·360 (2) | 0·135 (1) | 5·3 (5)* |
| H(13) | 0·200 (6) | 0·020 (2) | 0·380 (1) | 7·2 (6)* |
| H(11) | 0·558 (5) | 0·159 (2) | 0·542 (1) | 6·7 (6)* |
| H(2) | 1·098 (5) | 0·123 (2) | 0·033 (1) | 5·9 (5)* |
| H(3) | 1·330 (6) | −0·062 (2) | 0·070 (1) | 7·2 (6)* |
| H(4) | 1·234 (6) | −0·199 (2) | 0·209 (1) | 7·7 (6)* |
| H(5) | 0·945 (6) | −0·153 (2) | 0·317 (1) | 7·5 (6)* |
| H(6) | 0·697 (6) | 0·029 (2) | 0·275 (2) | 8·6 (7)* |
| H(19) | 0·520 (5) | 0·359 (2) | 0·287 (1) | 6·6 (6)* |
| H(20) | 0·773 (5) | 0·522 (2) | 0·200 (1) | 5·8 (5)* |
| H(21) | 0·744 (5) | 0·668 (2) | 0·246 (1) | 6·9 (6)* |
| H(22) | 0·464 (5) | 0·662 (2) | 0·380 (1) | 7·2 (6)* |
| H(23) | 0·212 (6) | 0·496 (2) | 0·454 (1) | 8·2 (7)* |

* Refined isotropically.

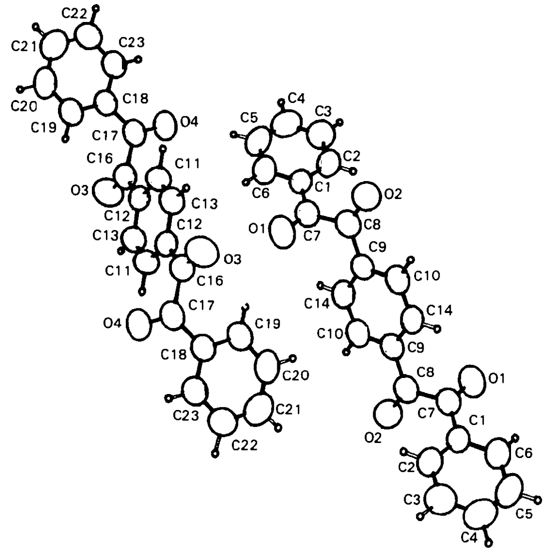

Fig. 1. *ORTEP* plot of the 2,2′-diphenyl-1,1′-(1,4-phenylene)-diethanedione molecules showing the atomic labeling scheme.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Numbers in parentheses are e.s.d.'s in the least significant digits.

| | | | |
|---|---|---|---|
| O(1)C(7) | 1·215 (3) | C(9)C(14) | 1·380 (3) |
| O(2)C(8) | 1·218 (3) | C(11)C(12) | 1·383 (3) |
| O(3)C(16) | 1·216 (3) | C(11)C(13) | 1·373 (3) |
| O(4)C(17) | 1·219 (3) | C(12)C(13) | 1·389 (3) |
| C(1)C(7) | 1·472 (3) | C(12)C(16) | 1·483 (3) |
| C(7)C(8) | 1·531 (3) | C(16)C(17) | 1·526 (3) |
| C(8)C(9) | 1·477 (3) | C(17)C(18) | 1·467 (3) |
| C(9)C(10) | 1·385 (3) | | |

| | | | |
|---|---|---|---|
| C(2)C(1)C(7) | 122·2 (2) | C(11)C(12)C(13) | 118·8 (2) |
| C(6)C(1)C(7) | 118·7 (2) | C(11)C(12)C(16) | 122·1 (2) |
| O(1)C(7)C(1) | 123·9 (2) | C(13)C(12)C(16) | 119·1 (2) |
| O(1)C(7)C(8) | 115·8 (2) | C(11)C(13)C(12) | 121·1 (2) |
| C(1)C(7)C(8) | 120·2 (2) | C(12)C(16)C(17) | 119·7 (2) |
| O(2)C(8)C(7) | 116·9 (2) | O(3)C(16)C(12) | 122·5 (2) |
| O(2)C(8)C(9) | 123·2 (2) | O(3)C(16)C(17) | 117·7 (2) |
| C(7)C(8)C(9) | 119·6 (2) | O(4)C(17)C(16) | 116·3 (2) |
| C(8)C(9)C(10) | 119·2 (2) | O(4)C(17)C(18) | 123·8 (2) |
| C(8)C(9)C(14) | 121·6 (2) | C(16)C(17)C(18) | 119·8 (2) |
| C(10)C(9)C(14) | 119·2 (2) | C(17)C(18)C(19) | 121·8 (2) |
| C(12)C(11)C(13) | 120·0 (2) | C(17)C(18)C(23) | 119·4 (2) |

Table 3. *Selected torsion angles* (°)

The e.s.d.'s for the torsion angles are in the range 0·4–0·5°.

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| O(1)C(7)C(1)C(2) | −176·7 | O(4)C(17)C(18)C(19) | 176·0 |
| O(1)C(7)C(1)C(6) | 2·6 | O(4)C(17)C(18)C(23) | −1·6 |
| C(2)C(1)C(7)C(8) | 7·4 | C(19)C(18)C(17)C(16) | −7·1 |
| C(6)C(1)C(7)C(8) | −173·3 | C(23)C(18)C(17)C(16) | 175·3 |
| O(1)C(7)C(8)O(2) | −111·7 | O(3)C(16)C(17)O(4) | 109·5 |
| O(1)C(7)C(8)C(9) | 63·3 | O(4)C(17)C(16)C(12) | −67·6 |
| O(2)C(8)C(7)C(1) | 64·6 | O(3)C(16)C(17)C(18) | −67·7 |
| C(7)C(8)C(9)C(10) | −167·3 | C(17)C(16)C(12)C(13) | 173·8 |
| C(7)C(8)C(9)C(14) | 13·5 | C(17)C(16)C(12)C(11) | −6·2 |
| O(2)C(8)C(9)C(10) | 7·3 | O(3)C(16)C(12)C(13) | −3·1 |
| O(2)C(8)C(9)C(14) | −171·8 | O(3)C(16)C(12)C(11) | 176·9 |
| C(1)C(7)C(8)C(9) | −120·4 | C(18)C(17)C(16)C(12) | 115·3 |

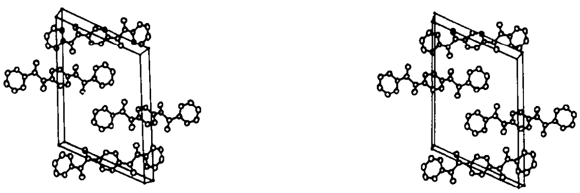

Fig. 2. Stereoview of the molecular packing in the unit cell.

1959; Kuchitsu, Fukuyama & Morino, 1968; Syed, Stevens & Klein, 1984).

A stereoscopic view of the contents of a unit cell is shown in Fig. 2. The structure consists of molecules packed in crystals through van der Waals forces. No unusually short intermolecular contacts were observed.

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*Acta Cryst.* (1984). C**40**, 1276–1278

# Structure of 3-Acetyl-5-(α-methylbenzylidene)-2,4-oxolanedione, $C_{14}H_{12}O_4$

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(*Received* 26 *January* 1984; *accepted* 21 *March* 1984)

**Abstract.** $M_r = 244{\cdot}2$, monoclinic, $P2_1/n$, $a = 4{\cdot}763\,(9)$, $b = 9{\cdot}785\,(5)$, $c = 24{\cdot}955\,(8)$ Å, $\beta = 92{\cdot}79\,(6)°$, $U = 1161{\cdot}67$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}40$ Mg m$^{-3}$, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}11$ mm$^{-1}$, $F(000) = 512{\cdot}00$, $T = 298$ K. Final $R = 0{\cdot}043$ for 991 observed reflections. The molecule exists as the *endo*-enolic tautomer. It is essentially planar with the phenyl group *cis* to the lactone moiety. There is an intramolecular O—H···O hydrogen bond of 2·562 (4) Å. Structural differences between the title compound and 3-acetyl-5-benzylidene-2,4-oxolanedione are discussed.

**Introduction.** The presence of the 3-acyl-2,4-oxolanedione ring† in several biologically active molecules [such as tetramycin (Keller-Juslen *et al.*, 1982), terrestric acid (Jacobsen, Reffstrop, Cox, Holker & Boll, 1978) and pulvinones (Pattenden, 1977)] has prompted extensive studies on the tautomeric population of simpler analogues such as 3-acetyl-2,4-oxolanediones. Fig. 1 shows the four possible tautomers, all of which have been detected by spectroscopic methods with 5-methyl and 3-acetyl-5-methylene-2,4-oxolanediones (Gelin & Pollet, 1980). In sharp contrast, 3-acetyl-5-benzylidene-2,4-oxolanedione exists as one single tautomer, unambiguously determined as the *endo*-enol form (Fig. 1, *A*) by a crystallographic study (Mazhar-ul-Haque, Ahmed, Pollet & Horne, 1984).

Continued interest led us to consider 3-acetyl-5-(α-methylbenzylidene)-2,4-oxolanedione. In addition to the still unravelled geometry about the exocyclic double bond (Gelin & Hartmann, 1976), the presence of an additional methyl group was envisioned to have a considerable steric effect on the overall structure of the ring system.

**Experimental.** Crystal *ca* 0·21 × 0·21 × 0·55 mm, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Mo $K\alpha$ radiation, 25 reflections ($9 < \theta < 19°$) used to obtain cell dimensions by least-squares refinement, intensities of 2556 reflections measured, using $\omega$–$2\theta$ scan, $\theta_{\max} = 25°$, range of $hkl$: −5 to 5, 0 to 11, 0 to 29; three standard reflections monitored at intervals of 9000 s showed no variation in intensities; 2045 unique and 991 observed reflections using $I > 2\sigma(I)$ criterion. Direct

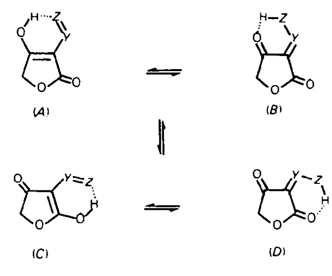

Fig. 1. Possible tautomeric forms for 3-substituted 2,4-oxolanediones.

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† 2,4-Oxolanedione is commonly referred to as 'tetronic acid'.

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