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3,5-Bis(4-methylbenzoyl)-2,6-bis(4-methylphenyl)-4*H*-pyran-4-one

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The title compound, $C_{35}H_{28}O_4$, is a tetrasubstituted 4*H*-pyran-4-one with 2,6-bis(*p*-tolyl) and 3,5-bis(*p*-toluyl) substituents. The pyran ring is almost planar; the planes of the toluyl substituents are approximately orthogonal to the pyran mean plane [both dihedral angles are equal to 86.2 (1)°], whereas the tolyl planes form with the latter much smaller dihedral angles of 32.5 (1) and 47.2 (1)°. The crystal structure features two intramolecular C—H$\cdots$O contacts and a C—H$\cdots\pi$(ring) interaction, with an H$\cdots$*Cg* distance of 2.70 (3) Å (*Cg* is the centroid of one of the benzene rings).

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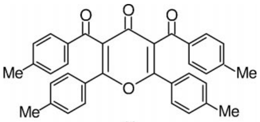
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.090
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The derivatives of the 4*H*-pyran-4-one heterocyclic system, also known as 4- or γ-pyrones, are usually quite stable crystalline compounds. It is noteworthy, however, that there are relatively few derivatives of non-fused pyrone among natural products, in contrast to the widespread occurrence of benzopyrone derivatives, also known as coumarins and chromones (Joule *et al.*, 1995). 4*H*-Pyran-4-ones and their various derivatives have been the subject of extensive studies because of their importance for a number of applications as well as their widespread biological significance (Kitagawa *et al.*, 1991; Zamocka *et al.*, 1991; Bransova *et al.*, 1995; Lowe *et al.*, 1997; Wakabayashi & Natori, 1999).



(I)

4-Aroyl-5-aryl-2,3-dihydro-2,3-furandiones represent easily accessible buiding blocks for the synthesis of heterocyclic systems (Kollenz *et al.*, 1991; Sarıpınar *et al.*, 2000; Hökelek *et al.*, 2002). It is known that thermal decomposition of the 2,3-dihydro-2,3-furandiones leads to to the formation of highly reactive diacylketene intermediates (Toung & Wentrup, 1992; Janoschek *et al.*, 1994; Yıldırım & İlhan, 1997; Stadler *et al.*, 2001). In particular, the thermolysis of 4-(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione at 448 K results in elimination of CO and formation of the intermediate ditoluylketene. In the absence of nucleophiles or suitable dienophiles, dimerization of acylketenes takes place as a special case of the hetero-Diels–Alder cycloaddition reaction (Clemens & Hyatt, 1985). In these reactions, the acylketene generally dimerizes and, after elimination of CO_2, gives the γ-pyrone derivative as a final stable product (Yıldırım & Koca, 2004). Under these conditions, the above mentioned ditoluylketene produces the title compound, (I), whose synthesis and structure are reported in the present paper.

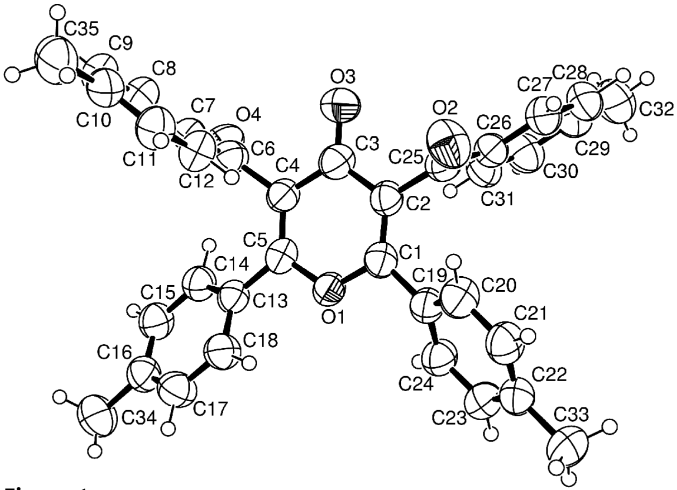


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title compound, showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

Compound (I) represents a tetrasubstituted-4*H*-pyran-4-one with 2,6-bis(*p*-tolyl) and 3,5-bis(*p*-toluyl) substituents (Fig. 1). The pyran ring O1/C1–C5 is planar within 0.025 Å; the mean planes of toluyl substituents C6/O4/C7–C12/C35 and C25/O2/C26–C32 are approximately orthogonal to the pyran plane [both dihedral angles are equal to 86.2 (1)°], whereas the tolyl planes C13–C18/C34 and C19–C24/C33 form with the latter much smaller dihedral angles of 32.5 (1) and 47.2 (1)°, respectively. Bond lengths and angles in the pyran ring are in good agreement with those reported in the literature for pyrans (Zhang *et al.*, 2003).

There are two weak intramolecular C—H···O contacts in the molecule of (I) (Table 2). Relatively short intermolecular distances between atom H27 and the atoms of the C13–C18 aromatic ring, as well as the peculiar orientation of the C27—H27 bond with respect to this ring, suggest the existence of a C—H···π interaction, which may play a significant role in the packing of the crystal (see Table 2). The packing of the molecules in the crystal is shown in Fig. 2.

Experimental

Dry 4-(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione (0.50 g, 1.63 mmol), readily available from di-(*p*-methylbenzoyl)methane and oxalyl chloride using a method similar to that reported by Ziegler *et al.* (1967) and Saalfrank *et al.* (1991), was heated to 448 K for 30–40 min. The residue was cooled to room temperature, triturated with ether, and then filtered and recrystallized from 1-butanol to give white crystals of (I) (yield 0.23 g, 55%; m.p. 520 K).

Crystal data

$C_{35}H_{28}O_4$
$M_r = 512.57$
Monoclinic, $P2_1/n$
$a = 10.8893$ (10) Å
$b = 10.6093$ (7) Å
$c = 23.629$ (2) Å
$\beta = 94.297$ (7)°
$V = 2722.1$ (4) Å^3
$Z = 4$
$D_x = 1.251$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7653 reflections
$\theta = 1.7$–24.1°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.32 × 0.26 × 0.13 mm

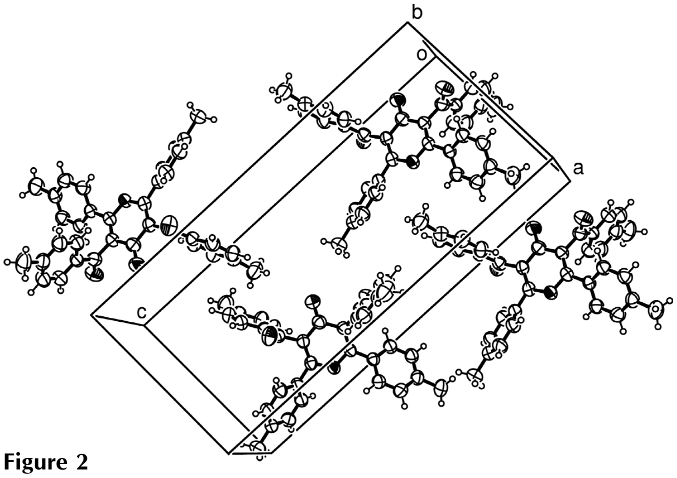


Figure 2
An *ORTEP*-3 (Farrugia, 1997) plot of the crystal packing of the title compound.

Data collection

Stoe IPDS-2 diffractometer
φ scans
Absorption correction: none
24 172 measured reflections
4785 independent reflections
2115 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\rm max} = 25.0°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.090$
$S = 1.01$
4785 reflections
417 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0137 (7)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.367 (3)	C2—C3	1.451 (3)
O1—C5	1.380 (2)	C2—C25	1.498 (3)
O2—C25	1.221 (3)	C3—C4	1.452 (3)
O3—C3	1.242 (2)	C4—C5	1.338 (3)
O4—C6	1.216 (3)	C4—C6	1.500 (3)
C1—C2	1.342 (3)	C5—C13	1.472 (3)
C1—C19	1.475 (3)		
C1—O1—C5	120.41 (18)	C5—C4—C3	120.9 (2)
C2—C1—O1	121.5 (2)	C4—C5—O1	121.0 (2)
C1—C2—C3	120.7 (2)	O4—C6—C7	122.3 (2)
O3—C3—C2	122.1 (2)	O4—C6—C4	121.4 (2)
O3—C3—C4	122.5 (2)	O2—C25—C26	121.4 (3)
C2—C3—C4	115.4 (2)	O2—C25—C2	119.2 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*3 denotes the centroid of the C13–C18 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O4	1.00 (2)	2.36 (2)	3.210 (3)	143.2 (19)
C20—H20···O2	0.92 (2)	2.56 (2)	3.216 (4)	129.1 (18)
C27—H27···*Cg*3$^{\rm i}$	1.11 (3)	2.70 (3)	3.792 (3)	169 (2)

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

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The components of the anisotropic displacement parameters in the direction of the bond were restrained during the final refinement to be 0.01 Å^2. H atoms, except those belonging to methyl groups, were located in a difference Fourier map and their positional and isotropic displacement parameters were refined. The C—H distances are in the range 0.90 (3)–1.11 (3) Å. H atoms belonging to the methyl groups were positioned geometrically (C—H = 0.96 Å) and included in the subsequent refinement in the riding model approximation [$U_{\rm iso}$($U_{\rm eq}$(methyl C)].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Bransova, J., Brtko, J., Uher, M. & Movotny, L. (1995). *Int. Biochem. Cell Biol.* **27**, 701–706; *Chem. Abstr.* **123**, 187959t.

Clemens, R. J. & Hyatt, J. A. (1985). *J. Org. Chem.* **50**, 2431–2439.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Hökelek, T., Sarıp.inar, E., Yıldırım, İ., Akkurt, M. & Akçamur, Y. (2002). *Acta Cryst.* E**58**, o30–o32.

Janoschek, R., Fabian, W. M. F. & Kollenz, G. (1994). *J. Comput. Chem.* **15**, 132–143.

Joule, J. A., Mills, K. & Smith, G. F. (1995). *Heterocyclic Chemistry*, 3rd ed., pp. 148–162. London: Chapman and Hall.

Kitagawa, M., Yamamoto, K., Katakura, S., Kanno, H., Yamada, K., Nagahara, T. & Tanaka, M. (1991). *Chem. Pharm. Bull.* **39**, 2681–2690; *Chem. Abstr.* (1992). **116**, 106034t.

Kollenz, G., Kappe, C. O. & El-Nabi, H. A. A. (1991). *Heterocycles*, **32**, 669–674.

Lowe, W., Bratter, S., Dietlich, C., Weber, M. & Luger, P. (1997). *J. Heterocycl. Chem.* **34**, 1173–1178.

Saalfrank, R. W., Lutz, T., Hörner, B., Gündel, J., Peters, K. & von Schnering, H. G. (1991). *Chem. Ber.* **124**, 2289–2295.

Sarıpınar, E., Güzel, Y., Önal, Z., İlhan, İ. Ö. & Akçamur, Y. (2000). *J. Chem. Soc. Pakistan*, **22**, 308–317.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stadler, A., Zangger, K., Belaj, F. & Kollenz, G. (2001). *Tetrahedron*, **57**, 6757–6763.

Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Toung, R. L. & Wentrup, C. (1992). *Tedrahedron Lett.* **48**, 7641–7654.

Wakabayashi, F. H. & Natori, Y. (1999). *Jpn Kokai Tokkyo JP*, 02 273 140; *Chem. Abstr.* (1991). **114**, 80308s.

Yıldırım, İ. & İlhan, İ. Ö. (1997). *J. Heterocycl. Chem.* **34**, 1047–1051.

Yıldırım, İ. & Koca, İ. (2004). *Asian J. Chem.* **16**. In the press.

Zamocka, J., Misikova, E. & Durinda, J. (1991). *Pharmazie*, **46**, 610; *Chem. Abstr.* (1992). **116**, 106031q.

Zhang, Y., Yuan, F., Xu, J., Wu, Q. & Huang, Z. (2003). *J. Chem. Crystallogr.* **33**, 165–168.

Ziegler, E., Eder, M., Belegratis, C. & Prewedourakis, E. (1967). *Monatsh. Chem.* **98**, 2249–2251.

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