Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# C—H···O, C—H···π and π–π interactions in three benzofuran-2-yl ketone derivatives

**Veysel T. Yilmaz,[a]* Canan Kazak,[b] Cumhur Kirilmis,[c] Murat Koca[c] and Frank W. Heinemann[d]**

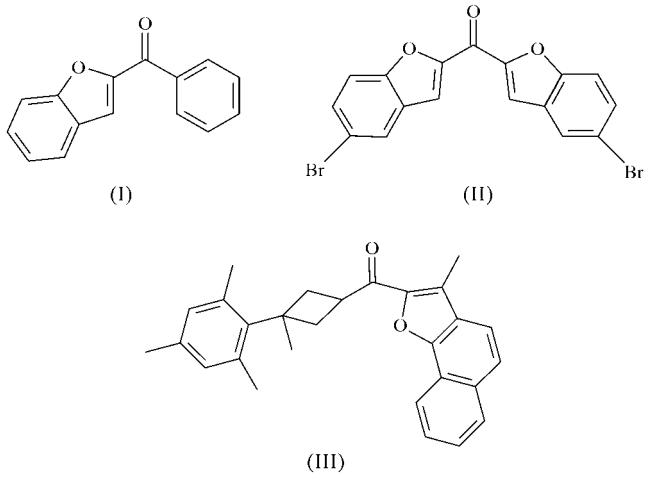
[a]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey, [b]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey, [c]Department of Chemistry, Faculty of Arts and Sciences, Firat University, 23169 Elazig, Turkey, and [d]Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany
Correspondence e-mail: vtyilmaz@omu.edu.tr

Received 12 May 2005
Accepted 20 May 2005
Online 22 June 2005

The molecules of 2-benzoyl-1-benzofuran, $C_{15}H_{10}O_2$, (I), interact through double C—H···O hydrogen bonds, forming dimers that are further linked by C—H···O, C—H···π and π–π interactions, resulting in a three-dimensional supramolecular network. The dihedral angle between the benzoyl and benzofuran fragments in (I) is 46.15 (3)°. The molecules of bis(5-bromo-1-benzofuran-2-yl) ketone, $C_{17}H_8Br_2O_3$, (II), exhibit $C_2$ symmetry, with the carbonyl group (C=O) lying along the twofold rotation axis, and are linked by a combination of C—H···O and C—H···π interactions and Br···Br contacts to form sheets. The stability of the molecular packing in 3-mesityl-3-methylcyclobutyl 3-methylnaphtho[1,2-*b*]furan-2-yl ketone, $C_{28}H_{28}O_2$, (III), arises from C—H···π and π–π stacking interactions. The fused naphthofuran moiety in (III) is essentially planar and makes a dihedral angle of 81.61 (3)° with the mean plane of the trimethylbenzene ring.

## Comment

Conventional 'strong and directional' hydrogen bonds, such as O—H···O, N—H···O and O—H···N, have long been recognized as being of fundamental importance in determining the supramolecular structure of organic solids (Desiraju & Steiner, 1999). In molecules lacking these hydrogen-bond donors and acceptors, other types of weak and less directional forces, such as C—H···O, C—H···π and π–π interactions, become important in generating supramolecular architectures (Desiraju & Steiner, 1999; Hunder & Sanders, 1990; Nishio *et al.*, 1998; Umezawa *et al.*, 1998; Calhorda, 2000). Since many natural benzofurans have physiological, pharmacological and toxic properties, there is continuing interest in their synthesis (Kappe *et al.*, 1997). Various benzofuran derivatives have been investigated as estrogen receptor ligands, because selective estrogen receptor modulators such as ralixofene have emerged as potential therapeutics for the prevention and treatment of osteoporosis (Sato *et al.*, 1999; Smith *et al.*, 2002). Amiodarone is a well known mitocondrial toxin containing a benzofuran ring. Amiodarone is used in the treatment and prophylaxis of both ventricular and superventricular arrhythmias, particularly in patients with heart insufficiency, because this compound has no significant negative inotropic effect (Spaniol *et al.*, 2001). Although the synthesis of 2-benzoyl-1-benzofuran, (I), is known (Demirayak *et al.*, 2002), a literature search showed that its structure has not yet been characterized. In addition to (I), we report the molecular and supramolecular structures of two new furan derivatives, namely bis(5-bromo-1-benzofuran-2-yl) ketone, (II), and 3-mesityl-3-methylcyclobutyl 3-methylnaphtho[1,2-*b*]furan-2-yl ketone, (III).




Views of the molecular structures of compounds (I)–(III), including the atom-numbering schemes, are shown in Figs. 1–3. Selected bond distances and angles are listed in Tables 1, 3 and 5. Compounds (I)–(III) consist mainly of a furan-2-yl moiety connected to another fragment by a carbonyl group. The C=O bond distances and the C—C—C bond angles between two fragments are similar in all three compounds. The carbonyl group is known to coordinate to metal ions rather easily, and the presence of the furan O atom adjacent to the carbonyl group in (I)–(III) makes these compounds potential bidentate chelating agents, as reported for lanthanum (Benassi *et al.* 1987). In (I), the fused benzofuran ring is essentially

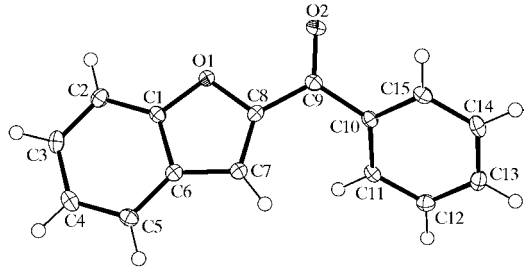



**Figure 1**
The molecular structure of (I), showing the atom-labeling scheme (50% probability displacement ellipsoids).

  DOI: 10.1107/S0108270105016185 

planar and makes a dihedral angle of 46.15 (3)° with the planar benzoyl ring. The conformation of compound (I) is similar to those of previously reported benzoylbenzofuran derivatives (Benassi *et al.*, 1987; Pei *et al.*, 2005). The crystal packing of (I) is governed by a set of weak intermolecular interactions. A dimer is formed *via* a C2—H2*A*···O1$^{i}$ hydrogen bond (see Table 2 for geometry and symmetry code), and the dimeric units are held together by a C7—H7*A*···O2$^{ii}$ hydrogen bond (Table 2), two C—H···$\pi$ interactions [C5—H5*A*···*Cg*2$^{iii}$ = 3.28 Å and C15—H15*A*···*Cg*1$^{iv}$ = 2.80 Å, where *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C10–C15 benzene rings; symmetry codes: (iii) $-x, 1-y, -z$; (iv) $1-x, 1-y, -z$] and two $\pi$–$\pi$ interactions [*Cg*1···*Cg*1$^{v}$ = 3.561 (1) Å and *Cg*2···*Cg*2$^{vi}$ = 3.776 (1) Å; symmetry codes: (v) $-x, -y, -z$; (vi) $1-x, 1-y, 1-z$], resulting in a three-dimensional supramolecular network (Fig. 4).

The molecules of (II) contain two symmetry-related planar bromobenzofuran rings attached to the carbonyl group (C9═O2), which is situated on the twofold rotation axis. The dihedral angle between the planes of the two equivalent bromobenzofuran ring moieties is 32.70 (4)°. In the packing of (II), the molecules are linked by a combination of a C—H···O hydrogen bond (Table 4) and a C—H···$\pi$ interaction [C2—H2*A*···*Cg*$^{viii}$ = 2.87 Å; *Cg* is the centroid of the C1–C6 ring; symmetry code: (viii) $x, 1-y, -\frac{1}{2}+z$]. Each molecule accepts two hydrogen bonds and donates two hydrogen bonds, thus forming chains running parallel to the crystallographic *b* axis. These chains are further linked by relatively short Br···Br contacts [Br···Br$^{ix}$ = 3.499 (2) Å; symmetry code: (ix) $\frac{1}{2}-x, \frac{5}{2}-y, -z$], resulting in a two-dimensional layer architecture (Fig. 5). The C—Br···Br angle is 146.85 (12) Å, and the Br···Br interactions play a crucial role in determining the crystal packing and compete successfully with other kinds of weak intermolecular interactions.

Compound (III) consists of a fused naphthofuran moiety (O2/C16–C27), a cyclobutane ring (C7/C9–C11) and a mesityl group (C1–C6/C12–C14). The naphthofuran and mesityl ring systems are essentially planar, and the dihedral angle between their planes is 81.86 (3)°, differing from the values reported for 1-(1-benzofuran-2-yl)-2-mesitylethanone [89.08 (4)°; Arıcı *et al.*, 2004] and (benzofuran-2-yl)(3-methyl-3-phenylcyclobutyl)methanone [73.63 (6)°; Yüksektepe *et al.*, 2004]. These differences may be explained by the presence of the different substituents in these compounds. The cyclobutane ring deviates significantly from planarity, with a puckering parameter ($q_2$) of 0.3972 (4) Å, and this finding is consistent with a similar benzofuran derivative containing a cyclobutane ring (Yüksektepe *et al.*, 2004). However, a nearly planar cyclobutane ring was also reported by Özdemir *et al.* (2004). The dihedral angles between the planes of the naphthofuran/cyclobutane and mesityl/cyclobutane ring systems are 52.15 (5) and 38.26 (8)°, respectively. In contrast to compounds (I) and (II), compound (III) does not exhibit C—H···O hydrogen bonds, and molecules of (III) are held together by C—H···$\pi$ and $\pi$–$\pi$ interactions (Fig. 6). There are three C—H···$\pi$ interactions between the H atoms of the

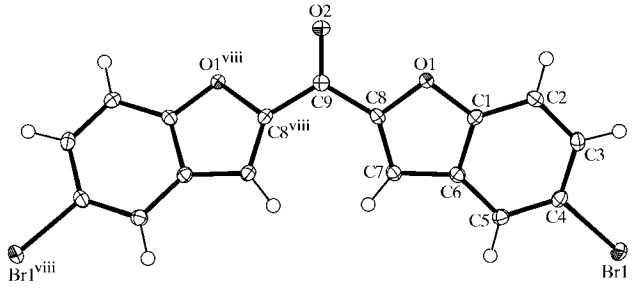



**Figure 2**
The molecular structure of (II), showing the atom-labeling scheme (50% probability displacement ellipsoids). [Symmetry code: (viii) $1-x, y, \frac{1}{2}-z$.]

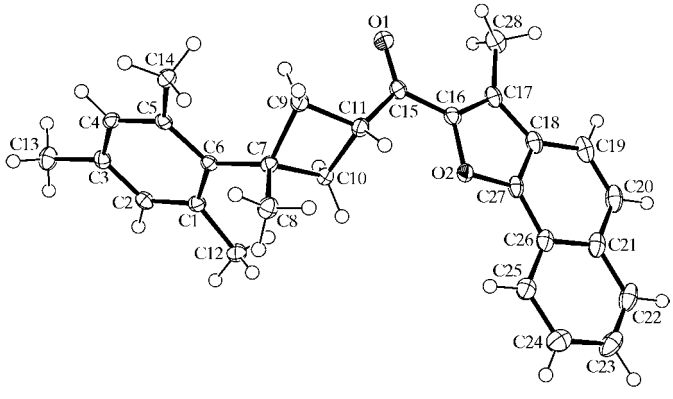



**Figure 3**
The molecular structure of (III), showing the atom-labeling scheme (50% probability displacement ellipsoids).

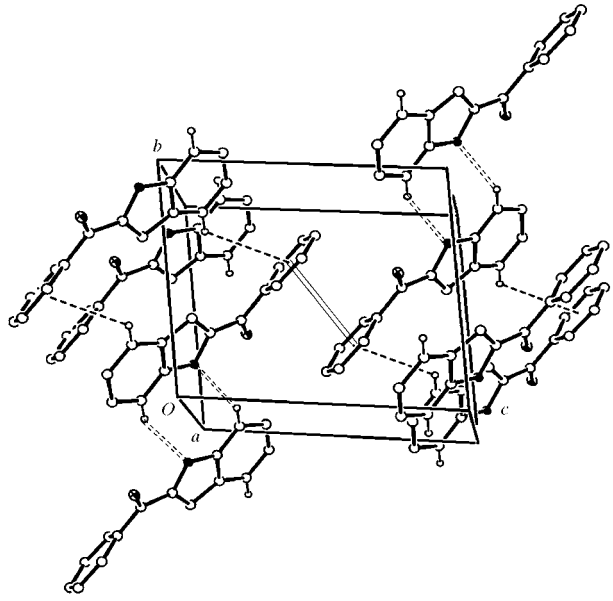



**Figure 4**
A packing diagram of (I). C—H···O interactions are indicated by double dashed lines and C—H···$\pi$ interactions by single dashed lines, while $\pi$–$\pi$ interactions are shown as double thin lines. O atoms are shown with octant shading.

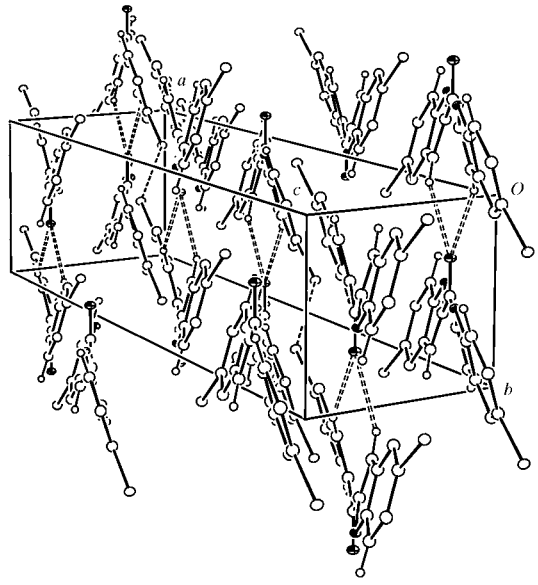



**Figure 5**
A packing diagram of (II). C—H···O interactions are represented as double dashed lines and Br···Br contacts are indicated by single dashed lines. O atoms are shown with octant shading.

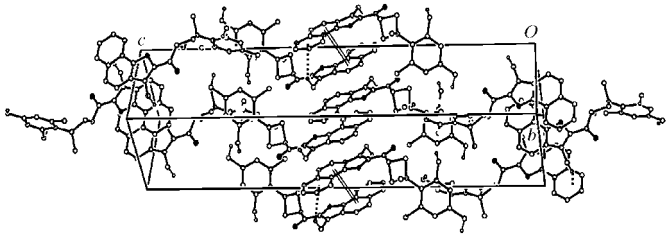



**Figure 6**
A packing diagram of (III), viewed along the crystallographic *b* axis. C—H···$\pi$ interactions are indicated by double dashed lines, while $\pi$–$\pi$ interactions are shown as double thin lines. O atoms are shown with octant shading.

methyl groups and the benzene rings [C13—H13*A*···*Cg*1$^{x}$ = 3.20 Å, C14—H14*B*···*Cg*1$^{xi}$ = 2.73 Å and C28—H28*A*···*Cg*2$^{iii}$ = 2.87 Å, where *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C21–C26 rings, respectively; symmetry codes: (x) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. In (III), the packing of the molecules is additionally reinforced by a $\pi$–$\pi$ stacking interaction between adjacent naphthalene rings, with a *Cg*1···*Cg*1$^{iii}$ distance of 3.695 (1) Å.

## Experimental

For the preparation of (I), a mixture of salicylaldehyde (12.21 g, 0.1 mol) and potassium carbonate (20.70 g, 0.15 mol) was stirred in dry acetone (250 ml) at room temperature for 2 h. A solution of phenacyl bromide (19.90 g, 0.1 mol) in dry acetone (20 ml) was added to this mixture. The resulting solution was poured into water (250 ml) and reprecipitated twice from water. Suitable crystals of (I) were obtained by recrystallizing the precipitate from acetone (yield 19.60 g, 89.1%). For the preparation of (II), a mixture of 5-bromo-2-hydroxybenzaldehyde (20.10 g, 0.1 mol) and potassium carbonate (20.70 g, 0.15 mol) was stirred in dry acetone (250 ml) at room temperature for 2 h. A solution of 1,3-dichloroacetone (6.35 g, 0.05 mol) in dry acetone (20 ml) was added and this mixture was poured into water (250 ml). The separated solid was filtered off, washed with water and recrystallized from tetrahydrofuran to give (II) (yield 33.8 g, 80.5%). For the preparation of (III), hydroxynaphthophenone (1.86 g, 10 mmol), potassium carbonate (2.07 g, 15 mmol) and dry tetrahydrofuran (100 ml) were placed in a 500 ml two-necked flask fitted with a reflux condenser, and the mixture was stirred for 1 h at room temperature. To this solution, a solution of 3-(2-chloro-1-oxoethyl)-1-mesityl-1-methylcyclobutane (2.64 g, 10 mmol) in acetonitrile (100 ml) was added dropwise over a period of about 30 min and the mixture was subsequently refluxed for 4 h. The progress of the reaction was monitored by IR spectroscopy. The mixture was allowed to cool to room temperature, and was then poured into water (500 ml) and reprecipitated twice from water. The solid was filtered off and recrystallized from tetrahydrofuran to obtain crystals of (III) (yield 2.85 g, 71.96%).

### Compound (I)

*Crystal data*

| | |
|---|---|
| $C_{15}H_{10}O_2$ | $Z = 2$ |
| $M_r = 222.23$ | $D_x = 1.402$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 6.1028$ (5) Å | Cell parameters from 36 reflections |
| $b = 8.8010$ (4) Å | $\theta = 6.0$–$20.0°$ |
| $c = 10.1195$ (6) Å | $\mu = 0.09$ mm$^{-1}$ |
| $\alpha = 97.700$ (4)° | $T = 100$ (2) K |
| $\beta = 93.710$ (6)° | Prism, colorless |
| $\gamma = 101.073$ (6)° | 0.34 × 0.31 × 0.28 mm |
| $V = 526.31$ (6) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker–Nonius KappaCCD diffractometer | $R_{int} = 0.070$ |
| $\varphi$ and $\omega$ scans | $\theta_{max} = 27.9°$ |
| 17534 measured reflections | $h = -8 \rightarrow 8$ |
| 2498 independent reflections | $k = -11 \rightarrow 11$ |
| 2049 reflections with $I > 2\sigma(I)$ | $l = -13 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.1374P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | |
| $wR(F^2) = 0.098$ | |
| $S = 1.06$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 2498 reflections | $\Delta\rho_{max} = 0.23$ e Å$^{-3}$ |
| 154 parameters | $\Delta\rho_{min} = -0.30$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| O2—C9 | 1.2257 (14) | C9—C10 | 1.4932 (16) |
| C8—C9 | 1.4678 (17) | | |
| C8—C9—C10 | 118.74 (10) | | |

**Table 2**
Hydrogen-bond geometry (Å, °) for (I).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2*A*···O1$^{i}$ | 0.95 | 2.57 | 3.4182 (14) | 149 |
| C7—H7*A*···O2$^{ii}$ | 0.95 | 2.55 | 3.1449 (14) | 121 |

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x-1, y, z$.

## Compound (II)

*Crystal data*

$C_{17}H_8Br_2O_3$
$M_r$ = 420.05
Monoclinic, $C2/c$
$a$ = 29.644 (2) Å
$b$ = 6.2536 (5) Å
$c$ = 7.8188 (8) Å
$\beta$ = 105.091 (6)°
$V$ = 1399.5 (2) Å$^3$
$Z$ = 4
$D_x$ = 1.994 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 89 reflections
$\theta$ = 6.0–20.0°
$\mu$ = 5.80 mm$^{-1}$
$T$ = 100 (2) K
Irregular, colorless
0.25 × 0.24 × 0.16 mm

*Data collection*

Bruker–Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min}$ = 0.262, $T_{max}$ = 0.398
19777 measured reflections
1814 independent reflections
1604 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.046
$\theta_{max}$ = 28.7°
$h = -40 \rightarrow 40$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.043
$S$ = 1.08
1814 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0084P)^2 + 2.8382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.32 e Å$^{-3}$

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Br1—C4 | 1.9010 (16) | C8—C9 | 1.473 (2) |
| O2—C9 | 1.223 (3) | | |
| O2—C9—C8 | 120.81 (10) | C8$^{vii}$—C9—C8 | 118.4 (2) |

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

**Table 4**
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C7—H7$A$···O2$^{xii}$ | 0.95 | 2.56 | 3.429 (2) | 151 |

Symmetry code: (xii) $x, y+1, z$.

## Compound (III)

*Crystal data*

$C_{28}H_{28}O_2$
$M_r$ = 396.50
Monoclinic, $P2_1/c$
$a$ = 7.3816 (3) Å
$b$ = 8.2874 (6) Å
$c$ = 34.591 (2) Å
$\beta$ = 95.487 (5)°
$V$ = 2106.4 (2) Å$^3$
$Z$ = 4
$D_x$ = 1.250 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 134 reflections
$\theta$ = 6.0–20.0°
$\mu$ = 0.08 mm$^{-1}$
$T$ = 100 (2) K
Block, colorless
0.34 × 0.25 × 0.16 mm

*Data collection*

Bruker–Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min}$ = 0.970, $T_{max}$ = 0.988
20365 measured reflections
4182 independent reflections
3360 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032
$\theta_{max}$ = 26.4°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -43 \rightarrow 43$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.106
$S$ = 1.03
4182 reflections
276 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 1.2434P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.26 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.25 e Å$^{-3}$

**Table 5**
Selected interatomic distances (Å) for (III).

| | | | |
|---|---|---|---|
| O1—C15 | 1.2237 (19) | C15—C16 | 1.473 (2) |
| C11—C15 | 1.505 (2) | | |

All H atoms were refined using a riding model, with C—H distances of 0.95–1.00 Å and $U_{iso}$(H) values of 1.2$U_{eq}$(C).

For all compounds, data collection: *COLLECT* (Bruker, 2002); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank Ondokuz Mayis and Firat Universities for the financial support given to the study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1211). Services for accessing these data are described at the back of the journal.

## References


Arıcı, C., Ülkü, D., Kirilmis, C., Koca, M. & Ahmedzade, M. (2004). *Acta Cryst.* E**60**, o941–o942.
Benassi, R., Folli, U., Iarossi, D., Schenetti, L., Taddei, F., Musatti, A. & Nardelli, M. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. 1443–1454.
Bruker (2002). *SADABS* (Version 2.06), *COLLECT* and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Calhorda, M. J. (2000). *Chem. Commun.* pp. 801–810.
Demirayak, S., Ucucu, U., Benkli, K., Gundogdu-Karaburun, N., Gundogdu-Karaburun, A., Akar, D., Karabacak, M. & Kiraz, N. (2002). *Il Farmaco,* **57**, 609–612.
Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond in Structural Chemistry and Biology.* Oxford University Press.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Hunder, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Kappe, C. O., Murphree, S. S. & Padwa, A. (1997). *Tetrahedron*, **53**, 14179–14233.
Nishio, M., Hirota, M. & Umezawa, Y. (1998). In *The C—H···π Interaction* (*Evidence, Nature and Consequences*). New York: Wiley-VCH.
Özdemir, N., Dinçer, M., Yilmaz, I. & Çukurovali, A. (2004). *Acta Cryst.* E**60**, o14–o16.
Pei, L.-X., Bu, X.-Z., Gu, L.-Q. & Ng, S. W. (2005). *Acta Cryst.* E**61**, o1081–o1082.
Sato, M., Grese, T. A., Dodge, J. A., Bryant, H. U. & Turner, C. H. (1999). *J. Med. Chem.* **42**, 1–24.
Smith, R. A., Chen, J., Mader, M. M., Muegge, I., Moehler, U., Katti, S., Marrero, D., Stirtan, W. G., Weaver, D. R., Xiao, H. & Carley, W. (2002). *Bioorg. Med. Chem. Lett.* **12**, 2875–2878.
Spaniol, M., Bracher, R., Ha, H. R., Follath, F. & Krahenbuhl, S. (2001). *J. Hepatol.* **35**, 628–636.
Umezawa, Y., Tsuboyama, S., Honda, K., Uzawa, J. & Nishio, M. (1998). *Bull. Chem. Soc. Jpn*, **71**, 1207–1213.
Yüksektepe, Ç., Saraçoglu, H., Koca, M., Çukurovali, A. & Çaliskan, N. (2004). *Acta Cryst.* C**60**, o509–o510.