organic papers

Gavin Blewett, Catharine Esterhuysen, Martin W. Bredenkamp and Klaus R. Koch*

Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

Correspondence e-mail: krk@sun.ac.za

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.048
wR factor = 0.105
Data-to-parameter ratio = 9.0

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

1,1-Dibenzoyl-3,3-dimethylurea

The molecules of 1,1-dibenzoyl-3,3-dimethylurea, $C_{17}H_{16}N_2O_3$, interact through an intermolecular C—H$\cdots$O hydrogen bond and several C—H$\cdots\pi$ interactions, resulting in a three-dimensional network.

Comment

As part of a systematic investigation into the N-acyl-N',N'-dialkylurea class of potential bidentate ligands, 1,1-dibenzoyl-3,3-dimethylurea, (I), was isolated as a significant by-product (24.6%) from the condensation of benzoyl chloride with 1,1-dimethylurea during the synthesis of N-benzoyl-N',N'-dimethylurea. Although the synthesis of (I) has been reported previously (Ravn *et al.*, 2003; Schroth *et al.*, 1985), a survey of the Cambridge Structural Database (Version 5.26, update of May 2005; Allen, 2002) showed that this structure has not yet been crystallographically characterized. We report here the crystal structure of (I). The molecular structure is shown in Fig. 1, and selected bond lengths and torsion angles are listed in Table 1.

(I)
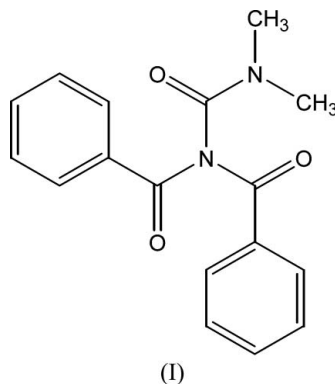
The C—N bond lengths C2—N1, N1—C3 and N1—C11 are all shorter than the reported general average C—N single bond length of 1.472 (5) Å (Allen *et al.*, 1987). However, C3—N2 is significantly shorter, at 1.324 (4) Å, thereby indicating partial double-bond character and restricted rotation around this bond.

The carbonyl group C3—O2 is acute relative to the C11—O3 and C2—O1 carbonyl groups, as illustrated by the pseudo-torsion angles O2—C3$\cdots$C11—O3 of 84.3 (4)° and O2—C3$\cdots$C2—O1 of 76.8 (3)°, while the carbonyl group C2—O1 is obtuse relative to carbonyl C11—O3, as illustrated by the pseudo-torsion angle O1—C2$\cdots$C11—O3 of 109.1 (3)°.

The crystal packing of (I) is governed by the intermolecular hydrogen interaction (as listed in Table 2), as well as through several face-to-edge C—H$\cdots\pi$ interactions. One-dimensional molecular chains extend along [100] as a result of a C7—
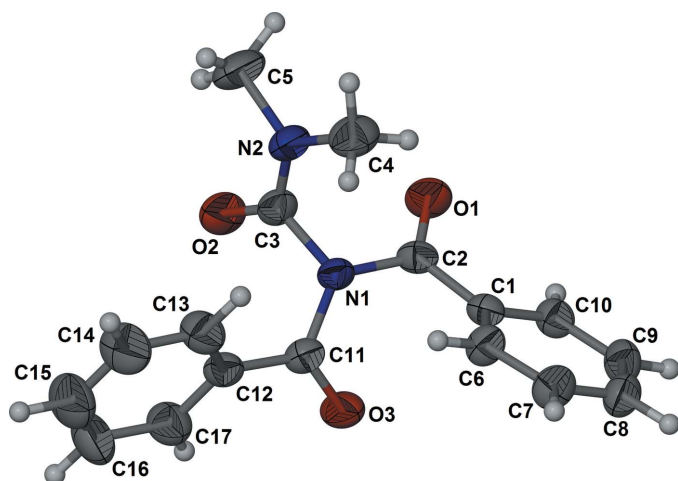
Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
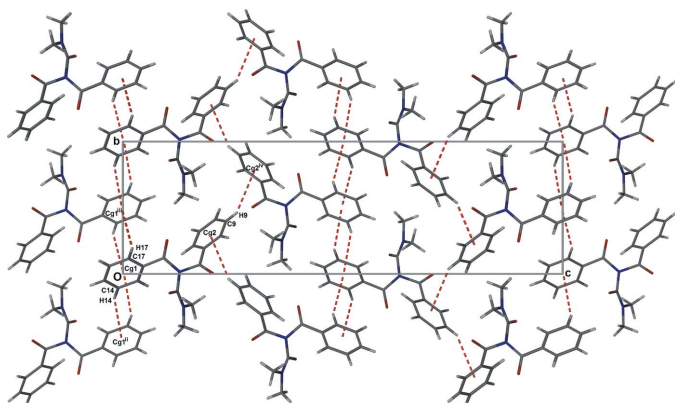

Figure 2
An extended packing diagram of (I), viewed along [100], indicating the C14—H14···$Cg1^{ii}$, C17—H17···$Cg1^{iii}$ and C9—H9···$Cg2^{iv}$ interactions as dashed lines. $Cg1$ and $Cg2$ are the centroids of the C12–C17 and C1/C6–C10 rings, repsectively. [Symmetry codes: (ii) $\frac{1}{2} + x$, $-y - \frac{1}{2}$, $-z$; (iii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$; (iv) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.]

H7···$O3^i$ intermolecular interaction [symmetry code: (i) $1 + x$, y, z].

Face-to-edge C—H···π interactions (illustrated in Fig. 2) [C14—H14···$Cg1^{ii}$ = 3.24 Å, C17—H17···$Cg1^{iii}$ = 3.13 Å, where $Cg1$ is the centroid of the C12–C17 benzoyl ring; symmetry codes: (ii) $\frac{1}{2} + x$, $-y - \frac{1}{2}$, $-z$; (iii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$] result in the formation of layers parallel to the (001) plane. A further C—H···π interaction [C9—H9···$Cg2^{iv}$ = 3.49 Å, where $Cg2$ is the centroid of the C1/C6–C10 benzoyl ring; symmetry code: (iv) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$] was observed in (I).

The C—H···π interactions observed here compare well with the C—H···π interactions observed for three benzoyl-furan-2-yl ketone derivatives (Yilmaz et al., 2005), as well as with ab initio calculated C—H···π interactions (Sinnokrot et al., 2002), which in turn correlate well with the mean distance between phenyl ring centroids of 5.05 Å for interacting side chains in proteins reported by Burley & Petsko (1985).

Experimental

Synthesis was carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. Triethylamine (3.3×10^{-2} mol), dissolved in anhydrous dichloromethane (10 ml), was added dropwise with stirring to a solution of benzoyl chloride (3.0×10^{-2} mol) dissolved in anhydrous dichloromethane (20 ml). After stirring at room temperature for 10 min, the above reaction mixture was added to a solution of N,N-dimethylurea (3.0×10^{-2} mol) dissolved in anhydrous dichloromethane (60 ml). The solution was warmed gently to 333 K for 1 h, cooled to room temperature and stirred overnight. Water (30 ml) was added and the crude product was extracted with chloroform (3×25 ml). The combined organic layers were washed with 3×25 ml of water, dried over $MgSO_4$ and filtered. The crude product was isolated as a white crystalline product under reduced vacuum and further purified by fractional crystallization from ethyl acetate and dichloromethane. Crystals suitable for single-crystal X-ray analysis were identified and isolated manually (overall yield 24.6%, based on N,N-dimethylurea). Elemental analysis calculated for $C_{17}H_{16}N_2O_3$: C 68.91, H 5.44, N 9.45%; found 68.53, H 5.42, N 9.97%.

Crystal data

$C_{17}H_{16}N_2O_3$	Mo $K\alpha$ radiation
$M_r = 296.32$	Cell parameters from 8844
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.002$ (3) Å	$\theta = 2.4$–$26.0°$
$b = 8.822$ (5) Å	$\mu = 0.09$ mm^{-1}
$c = 29.339$ (15) Å	$T = 100$ (2) K
$V = 1553.5$ (14) Å^3	Needle, colourless
$Z = 4$	$0.30 \times 0.10 \times 0.05$ mm
$D_x = 1.267$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD diffractometer	1803 independent reflections
	1483 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction: multi-scan (SADABS; Blessing, 1995; Sheldrick, 2002)	$\theta_{max} = 26.0°$
	$h = -7 \rightarrow 3$
	$k = -10 \rightarrow 10$
$T_{min} = 0.964$, $T_{max} = 0.996$	$l = -32 \rightarrow 36$
8844 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.2226P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	
$wR(F^2) = 0.105$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} = 0.009$
1803 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
201 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—C11	1.416 (3)	C1—C2	1.479 (4)
N1—C2	1.422 (3)	N2—C3	1.324 (4)
N1—C3	1.454 (4)	N2—C4	1.440 (4)
O3—C11	1.203 (3)	N2—C5	1.464 (4)
O1—C2	1.205 (3)	O2—C3	1.208 (4)
C11—C12	1.486 (4)		
O2—C3—C11—O3	84.3 (4)	O1—C2—C11—O3	109.1 (3)
O2—C3—C2—O1	76.8 (3)		

organic papers

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C7—H7···O3$^{\text{i}}$	0.95	2.47	3.349 (4)	153

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

All H atoms were placed in geometrically calculated positions, with C—H = 0.99 (for –CH$_2$–), 0.98 (for –CH$_3$) and 0.95 Å (for phenyl), and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ (for –CH$_3$ and phenyl) or $1.5U_{\text{eq}}(\text{parent})$ (for –CH$_3$). In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: *X-SEED*.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Atwood, J. L. & Barbour, L. J. (2003). *Cryst. Growth Des.* **3**, 3–8.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2001). *SMART*. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2002). *SAINT*. Version 6.36a. Bruker AXS Inc., Madison, Wisconsin, USA.
Burley, S. K. & Petsko, G. A. (1985). *Science*, **229**, 23–28.
Ravn, J., Ankersen, M., Begtrup, M. & Lau, J. F. (2003). *Tetrahedron Lett.* **44**, 6931–6935.
Schroth, W., Krieg, R., Kluge, H. & Gäbler, M. (1985). *Z. Chem.* **25**, 398–399.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. Version 2.05. University of Göttingen, Germany.
Sinnokrot, M. O., Valeev, E. F. & Sherrill, C. D. (2002). *J. Am. Chem. Soc.* **124**, 10887–10893.
Yilmaz, V. T., Kazak, C., Kirilmis, C., Koca, M. & Heinemann, F. W. (2005). *Acta Cryst.* C**61**, o438–o441.