

Wuxin Zou,^a Yu Gao,^a Teruki Sugiyama,^a Teruo Matsuura^b and Jiben Meng^{a*}^aDepartment of Chemistry, Nankai University, Tianjin 300071, People's Republic of China, and ^b21-26b Kawashima-Gondencho, Saikyoku, Kyoto 615-8195, JapanCorrespondence e-mail:
mengjiben@nankai.edu.cn

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.069
wR factor = 0.187
Data-to-parameter ratio = 12.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Succinimido 2-acetoxybenzoate

The title compound, $\text{C}_{13}\text{H}_{11}\text{NO}_6$, a modified aspirin, was characterized by ^1H NMR, solid-state IR and X-ray crystallographic techniques. The X-ray structure determination reveals that the twist of the acetyl group with respect to the phenyl ring is 12° less than that in aspirin. Also, the carboxyl plane is twisted out of the plane of the phenyl ring, probably due to the succinimide substitution. The crystal structure is stabilized by $\text{C}-\text{H}\cdots\text{O}$ and $\pi-\pi$ interactions.

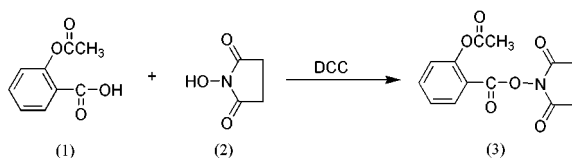
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Comment

Aspirin is used extensively as a painkiller, and it is also suggested to be effective against colorectal cancer (Heath *et al.*, 1994). The effects of aspirin on the aqueous solution structure of calf-thymus DNA and RNA have been reported (Neault *et al.*, 1996; Neault & Tajmir-Riahi, 1997). The title compound, (3), was prepared as part of our program to study the biological effects of an aspirin analog on calf-thymus DNA. Here we report the crystal structure of (3).



A perspective view of (3) with the atom labeling scheme is shown in Fig. 1. The bond lengths and angles in the aspirin moiety are in agreement with those reported for aspirin itself (Wheatley, 1964), except for the widening of the $\text{O4}-\text{C5}-\text{C6}$ angle to $127.2(4)^\circ$ and associated narrowing of the $\text{O3}-\text{C5}-\text{C6}$ angle to $110.4(3)^\circ$. The dihedral angle between the plane of the benzene ring and that of the acetyl group is $72.9(2)^\circ$, smaller than that in aspirin [84.8°]. The mean plane through atoms O3 , O4 , C5 and C6 is twisted from the plane of the phenyl ring by $34.3(2)^\circ$, while in aspirin the carboxyl plane is nearly coplanar with the phenyl ring. The twist might be due to the steric effect of the succinimide moiety. The dihedral angle between the succinimide moiety and the $\text{O3}-\text{O4}-\text{C5}-\text{C6}$ plane is $80.5(2)^\circ$.

Inversion-related molecules form dimeric pairs through $\text{C9}-\text{H9}\cdots\text{O2}^i$ hydrogen bonds; $\text{H9}\cdots\text{O2}^i$ 2.57, $\text{C9}\cdots\text{O2}^i$ 3.335 (6) \AA and $\text{C9}-\text{H9}\cdots\text{O2}^i$ 140° [symmetry code: (i) $1-x, -y, -z$]. Within the dimer, the two phenyl rings have a parallel-offset arrangement with a perpendicular separation of 3.434 (3) \AA , indicating $\pi-\pi$ -stacking interactions. The crystal structure is further stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between the dimers, forming a network structure [Fig. 2 and Table 2].

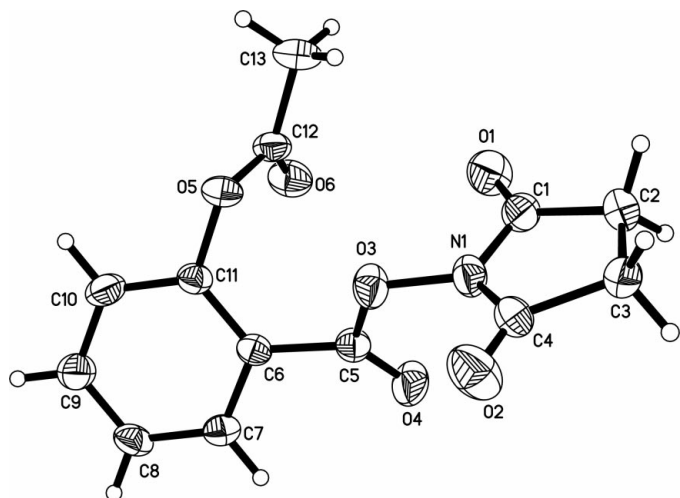


Figure 1
The molecular structure of (3), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

All purchased chemicals and solvents were reagent grade and used without further purification. Melting points were determined with a Yanagimoto MP-35 melting-point apparatus and were uncorrected. The $^1\text{H-NMR}$ spectra were measured with a Bruker AC-200 spectrometer, using tetramethylsilane as the internal standard. The solid-state IR spectra were recorded from KBr discs on a Bio-Rad FTS135 spectrophotometer.

A mixture of 0.36 g (2 mmol) of acetylsalicylic acid, 0.23 g (2 mmol) of N-hydroxysuccinimide and 0.61 g (3 mmol) of DCC (dicyclohexylcarbodiimide) in 20 ml of dried dichloromethane and 2 ml dried dimethylformamide (DMF) was stirred at room temperature for 24 h. After removing the insoluble solid by filtration, the filtrate was washed with 20 ml saturated hydrogen carbonate solution and then with 20×3 ml water and dried with MgSO_4 . The MgSO_4 was filtered off, the filtrate was concentrated and several drops of petroleum were added. After cooling, 0.22 g (36%) of fine colorless crystals of (3) were obtained, m.p. 360–362 K (uncorrected). $^1\text{H NMR}$ (CDCl_3): δ 2.31 (s, 3H, CH_3), 2.87 (s, 4H, 2CH_2), 7.17–8.14 (m, 4H, ArH). IR (cm^{-1} , KBr): 3527, 3520, 2996, 2956, 1775, 1738, 1607, 1484, 1450, 1360, 1282, 1204, 1156, 1102, 1064, 1002, 955, 916, 858, 820, 781, 749, 704, 642, 602.

Crystal data

$\text{C}_{13}\text{H}_{11}\text{NO}_6$	$D_x = 1.442 \text{ Mg m}^{-3}$
$M_r = 277.23$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 438 reflections
$a = 5.930$ (3) Å	$\theta = 2.3\text{--}22.5^\circ$
$b = 9.647$ (6) Å	$\mu = 0.12 \text{ mm}^{-1}$
$c = 22.331$ (9) Å	$T = 293$ (2) K
$\beta = 90.64$ (5)°	Block, colorless
$V = 1277.4$ (11) Å ³	$0.30 \times 0.25 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	2352 independent reflections
φ and ω scans	1428 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.084$
$T_{\text{min}} = 0.925$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 25.5^\circ$
5185 measured reflections	$h = -7 \rightarrow 6$
	$k = -8 \rightarrow 11$
	$l = -24 \rightarrow 26$

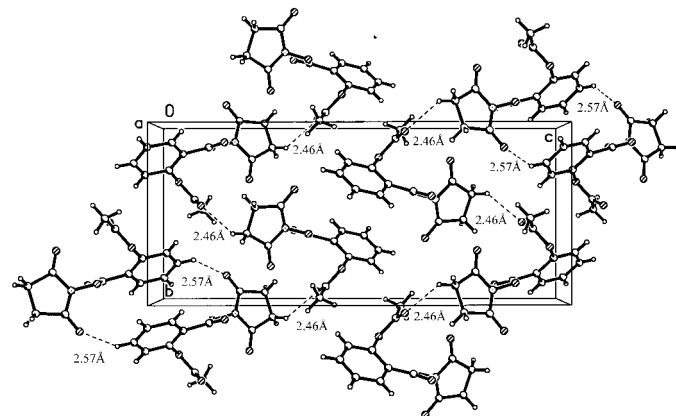


Figure 2
Molecular packing in the structure of (3), viewed along along the a axis.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 1.2437P]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.187$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
2352 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
183 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.052 (5)

Table 1

Selected geometric parameters (Å, °).

N1—C4	1.352 (5)	O3—C5	1.373 (4)
N1—C1	1.367 (5)	O4—C5	1.170 (4)
N1—O3	1.408 (4)	O5—C12	1.344 (5)
O1—C1	1.181 (5)	O5—C11	1.391 (4)
O2—C4	1.172 (5)	O6—C12	1.177 (5)
C4—N1—C1	117.5 (3)	C11—C6—C5	124.5 (3)
C4—N1—O3	120.3 (3)	C7—C6—C5	117.4 (3)
C1—N1—O3	120.9 (3)	O6—C12—C13	127.2 (4)
O4—C5—C6	127.2 (4)	O5—C12—C13	110.5 (4)
O3—C5—C6	110.4 (3)	C1—N1—O3—C5	85.7 (4)
C1—N1—O3—C5	85.7 (4)	O3—N1—C1—O1	−7.3 (6)
O3—N1—C1—O1	−7.3 (6)	C12—O5—C11—C6	73.7 (4)
N1—O3—C5—C6	−178.9 (3)	C11—O5—C12—O6	−0.1 (5)
O3—C5—C6—C11	35.2 (5)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C9—H9 \cdots O2 ⁱ	0.93	2.57	3.335 (6)	140
C2—H2B \cdots O6 ⁱⁱ	0.97	2.46	3.240 (6)	137
C3—H3A \cdots O1 ⁱⁱⁱ	0.97	2.59	3.490 (6)	155

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

All H atoms were placed geometrically and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{H})$ for methyl H atoms and $1.2U_{\text{eq}}$ for all other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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