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1-Methyl-4*H*-3,1-benzoxazine-2,4(1*H*)-dione

Nicholas P. Deifel,[a] Emily Cherney,[b] David A. Hunt[b] and Benny C. Chan[b]*

[a]Department of Chemistry, The George Washington University, 725 21st Street, NW, Washington, DC 20052, USA, and [b]Department of Chemistry, The College of New Jersey, 2000 Pennington Rd, Ewing, NJ 08628, USA
Correspondence e-mail: chan@tcnj.edu

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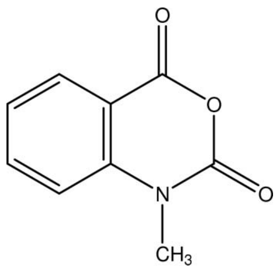
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.052; wR factor = 0.160; data-to-parameter ratio = 18.6.

In its crystal structure, the title compound, $C_9H_7NO_3$, forms π-stacked dimers, with a centroid–centroid distance of 3.475 (5) Å between the benzenoid and the 2,4 dicarbonyl oxazine rings. These dimers then form staircase-like linear chains through further π-stacking between the benzenoid rings [centroid–centroid distance of 3.761 (2) Å]. The methyl-H atoms are disordered due to rotation about the C—N bond and were modeled with equal occupancy.

Related literature

The title compound is a key intermediate for the synthesis of a variety of compounds, see: Coppola (1980); Kappe & Stadlbauer (1981); Shvekhgeimer (2001). Isatoaic anhydrides are important for the synthesis of a variety of commercial compounds. The crystal structures of two other isotoic anydrides have been reported: for the brominated 6-bromo-2*H*-3,1-benzoxazine-2,4(1*H*)-dione, see: Lubini & Wouters (1996) and for the unfunctionalized 2*H*-3,1-benzoxazine-2,4(1*H*)-dione, see: Kashino *et al.* (1978).



Experimental

Crystal data

$C_9H_7NO_3$
M_r = 177.16
Monoclinic, $P2_1/n$
a = 7.632 (2) Å
b = 8.818 (2) Å
c = 11.719 (3) Å
β = 93.599 (4)°
V = 787.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.5 × 0.5 × 0.4 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008) $T_{\min}$ = 0.902, $T_{\max}$ = 0.934
13548 measured reflections
2191 independent reflections
1532 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.160
S = 1.07
2191 reflections
118 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.20 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 e Å^{-3}

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (CrystalMaker, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2280).

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supplementary materials

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1-Methyl-4*H*-3,1-benzoxazine-2,4(1*H*)dione

N. P. Deifel, E. Cherney, D. A. Hunt and B. C. Chan

Comment

1-Methyl-2*H*-3,1- benzoxazine-2,4(1*H*)-dione (*N*-methylisatoic anhydride, **1**) is a key intermediate for the synthesis of a variety of compounds, such as agricultural chemicals, dyes/pigments flavors, fragrances, pharmaceuticals, ultraviolet absorbers, as well as esters, thioesters and amides of *N*-methylanthranilic acid (Kappe and Stadlbauer, 1981; Coppola, 1980; Shvekhgeimer, 2001). During the investigation of a novel *o*-aminoaryl oxazoline synthesis from the reaction of N-substituted isatoic anhydrides and 2-chloroethylamine hydrochloride in DMSO using an equimolar quantity of base, *o*-amino thiomethyl esters were observed as side products. In some cases, an *o*-amino thiomethyl ester was the major product (Hunt and Cherney, unpublished results).

The title compound is a planar molecule (Fig. 1). The bond distances are consistent with an aromatic system. The packing diagram, (Fig. 2) shows the aromatic rings form pi stacked dimers between the benzenoid ring and the 2,4 dicarbonyl oxazine ring, 3.475 (5) Å for both centroid to centroid distances (Crystalmaker ver. 2.1.2). The dimer forms a staircase-like linear chain through additional pi stacking between the benzenoid rings (3.761 (2) Å centroid to centroid).

Experimental

During the course of the reaction of N-substituted isatoic anhydrides and 2-chloroethylamine hydrochloride, unreacted 1 was isolated from products via silica gel chromatography in a 98:2 dichloromethane/methanol mobile phase. The 98:2 eluent was slowly evaporated to produce colorless rods and blocks of 1. A block was chosen for X-ray analysis, the rods gave the same unit cell as the block.

Refinement

The structure was solved using direct methods. The hydrogen atoms were positioned geometrically. A small improvement in the refinement occurred when the methyl hydrogens were modeled as 50% disordered due to free rotation about the C—N bond.

Figures

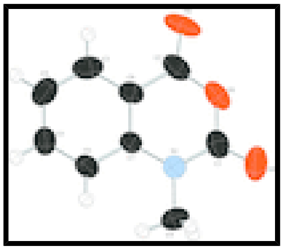

Fig. 1. Thermal ellipsoid plot at 50% probability, the disordered hydrogen atoms were removed for clarity.

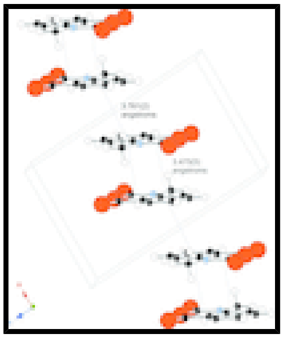

Fig. 2. The packing diagram viewed along the b axis shows π-stacked dimers that are separated by 3.475 (5) Å (centroid to centroid shown as a blue dashed line). A staircase-like linear chain forms from additional π-stacking through the bezenoid rings (3.761 (2) Å). Oxygen atoms are shown in red, nitrogen atoms in blue, carbon atoms in red and the hydrogen atoms in white.

1-Methyl-4*H*-3,1-benzoxazine-2,4(1*H*)dione

Crystal data

$C_9H_7NO_3$

$M_r = 177.16$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 7.632$ (2) Å

$b = 8.818$ (2) Å

$c = 11.719$ (3) Å

$\beta = 93.599$ (4)°

$V = 787.1$ (4) Å^3

$Z = 4$

$F(000) = 368$

$D_x = 1.495$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5577 reflections

$\theta = 5.8–59.2°$

$\mu = 0.11$ mm^{-1}

$T = 296$ K

Block, colorless

0.5 × 0.5 × 0.4 mm

Data collection

Bruker APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

graphite

ω and φ scans

Absorption correction: multi-scan (SADABS; Bruker, 2008)

$T_{min} = 0.902$, $T_{max} = 0.934$

13548 measured reflections

2191 independent reflections

1532 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$

$\theta_{max} = 30.1°$, $\theta_{min} = 2.9°$

$h = -10 \rightarrow 10$

$k = -9 \rightarrow 12$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.160$

$S = 1.07$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.1822P]$

where $P = (F_o^2 + 2F_c^2)/3$

2191 reflections	$(\Delta/\sigma)_{\max} < 0.001$
118 parameters	$\Delta\rho_{\max} = 0.20$ e Å^{-3}
0 restraints	$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
O3	0.9373 (2)	0.59606 (17)	0.17004 (14)	0.0830 (5)	
O2	0.9649 (2)	1.0762 (2)	0.27147 (12)	0.0906 (6)	
O1	0.93997 (16)	0.83752 (18)	0.21847 (10)	0.0668 (4)	
N1	0.80524 (17)	0.76241 (15)	0.04367 (11)	0.0494 (3)	
C1	0.8953 (2)	0.7229 (2)	0.14315 (15)	0.0576 (4)	
C2	0.9119 (2)	0.9903 (2)	0.19846 (14)	0.0596 (5)	
C3	0.7855 (2)	1.1789 (2)	0.06087 (16)	0.0607 (5)	
H3	0.8214	1.2561	0.1112	0.073*	
C4	0.6984 (3)	1.2139 (2)	−0.04182 (18)	0.0662 (5)	
H4	0.6748	1.3144	−0.0613	0.079*	
C5	0.6463 (2)	1.0989 (2)	−0.11575 (15)	0.0591 (4)	
H5	0.5872	1.1228	−0.1853	0.071*	
C6	0.6794 (2)	0.95018 (19)	−0.08922 (13)	0.0488 (4)	
H6	0.6430	0.8742	−0.1404	0.059*	
C7	0.76789 (17)	0.91246 (16)	0.01464 (11)	0.0402 (3)	
C8	0.82028 (18)	1.02777 (18)	0.08998 (12)	0.0462 (4)	
C9	0.7552 (3)	0.6393 (2)	−0.0348 (2)	0.0780 (6)	
H9A	0.6927	0.6799	−0.1016	0.117*	0.50
H9B	0.6811	0.5691	0.0022	0.117*	0.50
H9C	0.8587	0.5878	−0.0567	0.117*	0.50
H9D	0.7956	0.5446	−0.0025	0.117*	0.50
H9E	0.8072	0.6554	−0.1063	0.117*	0.50
H9F	0.6297	0.6367	−0.0474	0.117*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0874 (10)	0.0758 (10)	0.0840 (10)	0.0213 (8)	−0.0077 (8)	0.0243 (8)
O2	0.0825 (10)	0.1184 (14)	0.0673 (9)	−0.0039 (9)	−0.0231 (7)	−0.0386 (9)

O1	0.0639 (7)	0.0889 (10)	0.0455 (6)	0.0043 (7)	−0.0147 (5)	0.0028 (6)
N1	0.0527 (7)	0.0442 (7)	0.0499 (7)	0.0013 (5)	−0.0079 (5)	−0.0009 (5)
C1	0.0515 (9)	0.0646 (11)	0.0558 (9)	0.0072 (7)	−0.0025 (7)	0.0104 (8)
C2	0.0470 (8)	0.0819 (13)	0.0489 (8)	−0.0014 (8)	−0.0060 (6)	−0.0148 (8)
C3	0.0554 (9)	0.0509 (10)	0.0758 (11)	−0.0090 (7)	0.0049 (8)	−0.0169 (8)
C4	0.0670 (11)	0.0474 (10)	0.0839 (13)	−0.0007 (8)	0.0030 (9)	0.0084 (8)
C5	0.0597 (10)	0.0622 (11)	0.0549 (9)	0.0018 (8)	−0.0015 (7)	0.0128 (8)
C6	0.0505 (8)	0.0531 (9)	0.0418 (7)	−0.0028 (7)	−0.0048 (6)	−0.0009 (6)
C7	0.0368 (6)	0.0443 (8)	0.0393 (6)	−0.0016 (5)	0.0001 (5)	−0.0022 (5)
C8	0.0390 (7)	0.0530 (9)	0.0463 (7)	−0.0044 (6)	0.0003 (5)	−0.0095 (6)
C9	0.0984 (15)	0.0469 (10)	0.0854 (14)	0.0068 (10)	−0.0219 (11)	−0.0154 (9)

Geometric parameters (Å, °)

O3—C1	1.201 (2)	C4—H4	0.9300
O2—C2	1.194 (2)	C5—C6	1.368 (2)
O1—C1	1.371 (2)	C5—H5	0.9300
O1—C2	1.382 (3)	C6—C7	1.3944 (19)
N1—C1	1.361 (2)	C6—H6	0.9300
N1—C7	1.3912 (19)	C7—C8	1.3888 (19)
N1—C9	1.459 (2)	C9—H9A	0.9600
C2—C8	1.450 (2)	C9—H9B	0.9600
C3—C4	1.373 (3)	C9—H9C	0.9600
C3—C8	1.397 (3)	C9—H9D	0.9600
C3—H3	0.9300	C9—H9E	0.9600
C4—C5	1.376 (3)	C9—H9F	0.9600
C1—O1—C2	125.43 (13)	C7—C8—C3	120.04 (14)
C1—N1—C7	122.51 (14)	C7—C8—C2	119.62 (15)
C1—N1—C9	116.62 (15)	C3—C8—C2	120.34 (15)
C7—N1—C9	120.81 (13)	N1—C9—H9A	109.5
O3—C1—N1	125.14 (18)	N1—C9—H9B	109.5
O3—C1—O1	117.80 (16)	H9A—C9—H9B	109.5
N1—C1—O1	117.06 (15)	N1—C9—H9C	109.5
O2—C2—O1	117.05 (18)	H9A—C9—H9C	109.5
O2—C2—C8	127.4 (2)	H9B—C9—H9C	109.5
O1—C2—C8	115.59 (14)	N1—C9—H9D	109.5
C4—C3—C8	120.15 (16)	H9A—C9—H9D	141.1
C4—C3—H3	119.9	H9B—C9—H9D	56.3
C8—C3—H3	119.9	H9C—C9—H9D	56.3
C3—C4—C5	119.44 (17)	N1—C9—H9E	109.5
C3—C4—H4	120.3	H9A—C9—H9E	56.3
C5—C4—H4	120.3	H9B—C9—H9E	141.1
C6—C5—C4	121.41 (16)	H9C—C9—H9E	56.3
C6—C5—H5	119.3	H9D—C9—H9E	109.5
C4—C5—H5	119.3	N1—C9—H9F	109.5
C5—C6—C7	119.98 (15)	H9A—C9—H9F	56.3
C5—C6—H6	120.0	H9B—C9—H9F	56.3
C7—C6—H6	120.0	H9C—C9—H9F	141.1
C8—C7—N1	119.63 (13)	H9D—C9—H9F	109.5

C8—C7—C6	118.98 (14)	H9E—C9—H9F	109.5
N1—C7—C6	121.39 (13)		

Fig. 1

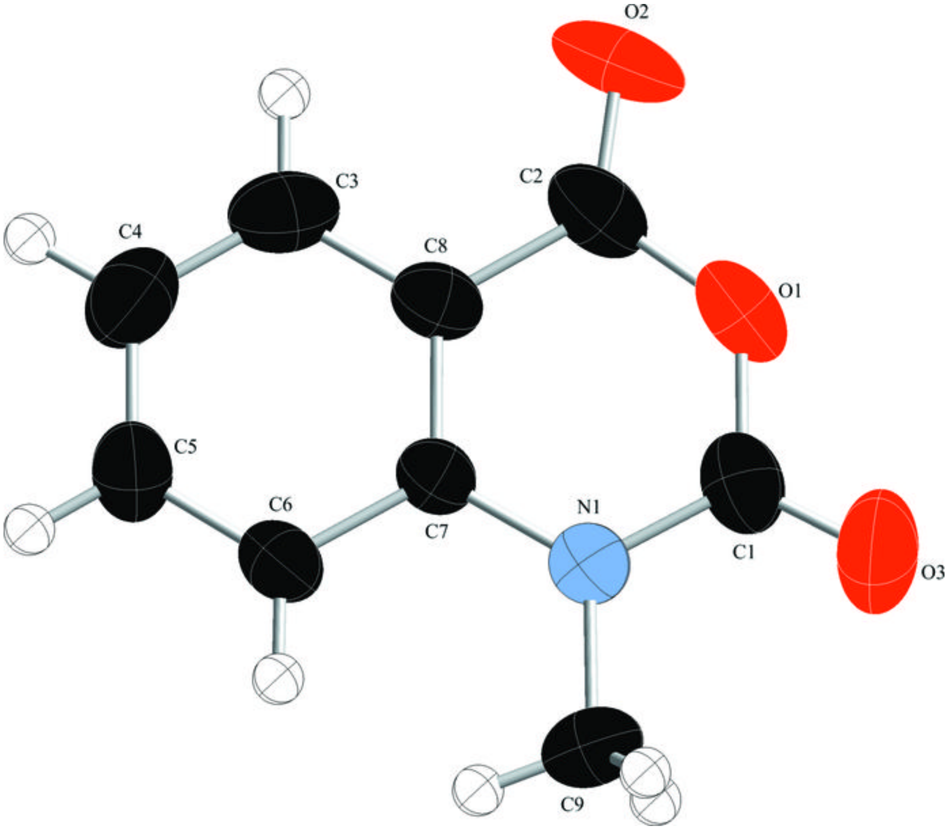

Fig. 2