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5-[(2-Chloro-4-nitroanilino)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione

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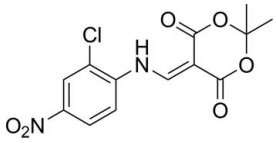
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.104; data-to-parameter ratio = 14.2.

In the title compound, $C_{13}H_{11}ClN_2O_6$, the dihedral angles between the benzene ring and the aminomethylene unit and between the aminomethylene group and the dioxane ring are 8.19 (14) and 1.39 (17)°, respectively. The dioxane ring has a half-boat conformation, in which the C atom between the dioxane O atoms is 0.662 (4)Å out of the plane through the remaining ring atoms. Intramolecular N—H···O and N—H···Cl interactions occur.

Related literature

For the synthesis of related compounds, see: Cassis *et al.* (1985). For the biological activity of related compounds, see: Griera *et al.* (1997); Darque *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{11}ClN_2O_6$ M_r = 326.69
Monoclinic, $P2_1/c$
a = 13.5850 (5) Å
b = 5.04379 (14) Å
c = 21.0272 (7) Å
β = 104.427 (4)°
V = 1395.35 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 293 K
0.40 × 0.40 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
T_{min} = 0.984, T_{max} = 1.0
6136 measured reflections
2853 independent reflections
2141 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.04
2853 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl1	0.86	2.46	2.9328 (15)	115
N2—H2···O3	0.86	1.99	2.670 (2)	136

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

We thank the Analytical and Testing Center of Sichuan University for the X-ray measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2269).

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supporting information

Acta Cryst. (2011). E**67**, o392 [doi:10.1107/S160053681100095X]

5-[(2-Chloro-4-nitroanilino)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione

Xian-Qiu Lan, Xiao-Feng Zhang, Ying-Hong Yang and You-Fu Luo

S1. Comment

The 4(1*H*)quinolone are of great importance owing to their wide biological properties (Griera *et al.*, 1997; Darque *et al.*,2009). 5-{[(2-Chloro-4-nitrophenyl)amino]methylene}-2,2-dimethyl-1,3-dioxane- 4,6-dione is one of the key intermediates in our synthetic investigations of new 4(1*H*)quinolone derivatives. We report here its crystal structure. The title compound is approximately planar, the dihedral angles between the benzene ring and the aminomethylene unit and between the aminomethylene group and the dioxane ring are 8.19 (14)° and 1.39 (17)°, respectively. The dioxane ring has a half-boat conformation, in which the C atom between the dioxane O atoms is 0.6615 (35) Å out of the plane (Figure 1.). In the molecule, there are intramolecular N—H···O and N—H···Cl interactions (Table 1.).

S2. Experimental

An ethanol solution (50 ml) of 2,2–dimethyl–1,3–dioxane–4,6–dione (1.44 g, 10 mmol) and triethoxymethane (1.78 g, 12 mmol) was heated to reflux for 2.5 h, then the 2-chloro-4-nitroaniline(1.72 g, 10 mmol) was added into the solution. The mixture was heated under reflux for another 8 h and then filtered. The precipitate was recrystallized from ethanol, giving the title compound. Crystals suitable for X-ray analysis were obtained by slow evaporation from a solution of ethanol.

S3. Refinement

The H-atom of N was located in a difference Fourier map and free refined: N—H = 0.86 Å. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic,*C*—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

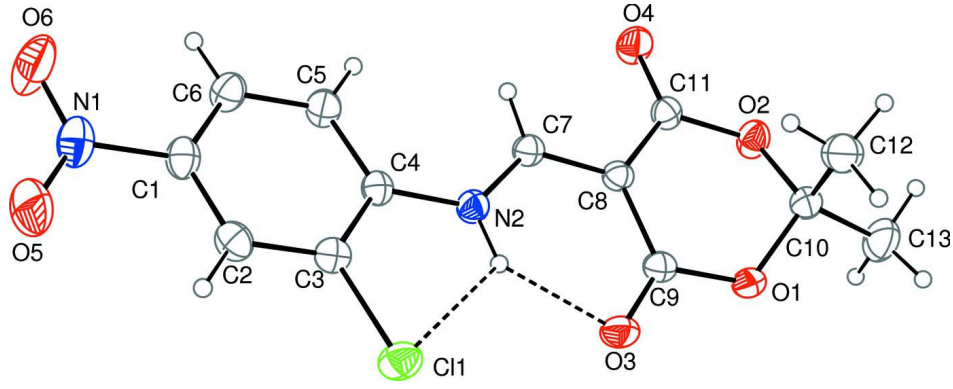

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. The intramolecular hydrogen bonds are shown as a dashed lines.

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Crystal data

$C_{13}H_{11}ClN_2O_6$
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Hall symbol: -P 2ybc
$a = 13.5850\ (5)$ Å
$b = 5.04379\ (14)$ Å
$c = 21.0272\ (7)$ Å
$\beta = 104.427\ (4)°$
$V = 1395.35\ (8)$ Å^3
$Z = 4$
$F(000) = 672$
$D_x = 1.555$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
Cell parameters from 2432 reflections
$\theta = 3.0–29.2°$
$\mu = 0.31$ mm^{-1}
$T = 293$ K
Block, colorless
0.40 × 0.40 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0874 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
$T_{min} = 0.984$, $T_{max} = 1.0$
6136 measured reflections
2853 independent reflections
2141 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.1°$
$h = -16\rightarrow16$
$k = -6\rightarrow6$
$l = -25\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.104$
$S = 1.04$
2853 reflections
201 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1291P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Experimental. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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_{iso}*/U_{eq}
Cl1	0.11303 (4)	0.78022 (10)	0.26632 (2)	0.05062 (18)
O1	−0.23464 (10)	0.7514 (2)	0.04172 (7)	0.0446 (4)

O2	−0.24014 (10)	0.4073 (3)	−0.03503 (6)	0.0469 (4)
O3	−0.09905 (11)	0.8273 (3)	0.12205 (7)	0.0517 (4)
O4	−0.10943 (10)	0.1444 (3)	−0.03156 (7)	0.0509 (4)
O5	0.46457 (14)	0.3369 (4)	0.35706 (9)	0.0855 (6)
O6	0.48067 (14)	0.0203 (4)	0.29216 (9)	0.0910 (6)
N1	0.43369 (14)	0.2060 (4)	0.30716 (10)	0.0592 (5)
N2	0.05320 (11)	0.4776 (3)	0.14363 (7)	0.0360 (4)
H2	0.0263	0.6155	0.1565	0.043*
C1	0.33473 (15)	0.2739 (4)	0.26352 (9)	0.0432 (5)
C2	0.27826 (15)	0.4698 (4)	0.28308 (9)	0.0431 (5)
H2A	0.3024	0.5569	0.3229	0.052*
C3	0.18530 (14)	0.5341 (3)	0.24251 (9)	0.0377 (4)
C4	0.14835 (13)	0.4042 (3)	0.18250 (8)	0.0337 (4)
C5	0.20803 (15)	0.2071 (4)	0.16447 (9)	0.0421 (5)
H5	0.1847	0.1193	0.1247	0.051*
C6	0.30095 (15)	0.1410 (4)	0.20485 (10)	0.0455 (5)
H6	0.3404	0.0086	0.1928	0.055*
C7	−0.00122 (13)	0.3622 (3)	0.08932 (8)	0.0336 (4)
H7	0.0254	0.2132	0.0736	0.040*
C8	−0.09479 (13)	0.4525 (3)	0.05552 (8)	0.0328 (4)
C9	−0.14016 (14)	0.6847 (3)	0.07640 (9)	0.0373 (4)
C10	−0.29653 (14)	0.5492 (4)	0.00333 (10)	0.0437 (5)
C11	−0.14546 (14)	0.3172 (4)	−0.00500 (9)	0.0359 (4)
C12	−0.33222 (18)	0.3613 (4)	0.04848 (13)	0.0656 (7)
H12B	−0.3779	0.2337	0.0229	0.098*
H12C	−0.3668	0.4590	0.0756	0.098*
H12A	−0.2748	0.2713	0.0758	0.098*
C13	−0.38047 (18)	0.6932 (5)	−0.04496 (12)	0.0695 (7)
H13B	−0.3514	0.8249	−0.0678	0.104*
H13C	−0.4245	0.7774	−0.0218	0.104*
H13A	−0.4188	0.5687	−0.0760	0.104*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0589 (4)	0.0482 (3)	0.0464 (3)	0.0072 (2)	0.0162 (3)	−0.0079 (2)
O1	0.0400 (8)	0.0317 (6)	0.0572 (9)	0.0054 (6)	0.0025 (7)	−0.0053 (6)
O2	0.0393 (8)	0.0582 (8)	0.0405 (8)	0.0068 (6)	0.0048 (6)	−0.0090 (7)
O3	0.0527 (9)	0.0407 (7)	0.0556 (9)	0.0058 (6)	0.0018 (7)	−0.0167 (7)
O4	0.0477 (9)	0.0585 (9)	0.0464 (8)	0.0064 (7)	0.0118 (7)	−0.0192 (7)
O5	0.0679 (12)	0.1027 (14)	0.0660 (11)	0.0073 (10)	−0.0210 (10)	−0.0129 (11)
O6	0.0689 (12)	0.1144 (15)	0.0783 (13)	0.0444 (12)	−0.0031 (10)	0.0001 (11)
N1	0.0447 (11)	0.0748 (13)	0.0522 (12)	0.0057 (10)	0.0013 (9)	0.0098 (10)
N2	0.0349 (8)	0.0370 (8)	0.0364 (9)	0.0019 (7)	0.0092 (7)	−0.0035 (7)
C1	0.0369 (11)	0.0526 (12)	0.0382 (11)	0.0015 (9)	0.0060 (9)	0.0074 (9)
C2	0.0462 (12)	0.0481 (11)	0.0327 (10)	−0.0039 (9)	0.0051 (9)	−0.0018 (9)
C3	0.0409 (11)	0.0385 (10)	0.0358 (10)	−0.0014 (8)	0.0136 (9)	0.0005 (8)
C4	0.0317 (10)	0.0373 (9)	0.0333 (10)	−0.0022 (7)	0.0107 (8)	0.0030 (8)

C5	0.0404 (11)	0.0500 (11)	0.0357 (11)	0.0028 (9)	0.0090 (9)	−0.0051 (9)
C6	0.0412 (11)	0.0497 (11)	0.0467 (12)	0.0067 (9)	0.0128 (9)	−0.0008 (10)
C7	0.0340 (10)	0.0351 (9)	0.0340 (10)	−0.0001 (8)	0.0130 (8)	−0.0005 (8)
C8	0.0342 (10)	0.0314 (9)	0.0344 (10)	−0.0008 (7)	0.0115 (8)	−0.0017 (8)
C9	0.0388 (10)	0.0308 (9)	0.0416 (11)	−0.0010 (8)	0.0086 (9)	0.0004 (8)
C10	0.0365 (10)	0.0413 (10)	0.0529 (12)	0.0015 (8)	0.0099 (9)	−0.0124 (9)
C11	0.0339 (10)	0.0400 (10)	0.0356 (10)	−0.0012 (8)	0.0120 (8)	−0.0014 (9)
C12	0.0596 (15)	0.0528 (13)	0.0971 (19)	−0.0072 (11)	0.0431 (14)	−0.0094 (13)
C13	0.0470 (14)	0.0787 (17)	0.0703 (16)	0.0174 (12)	−0.0089 (12)	−0.0148 (13)

Geometric parameters (Å, º)

Cl1—C3	1.7321 (19)	C3—C4	1.399 (2)
O1—C9	1.351 (2)	C4—C5	1.394 (2)
O1—C10	1.436 (2)	C5—H5	0.9300
O2—C10	1.434 (2)	C5—C6	1.375 (3)
O2—C11	1.362 (2)	C6—H6	0.9300
O3—C9	1.218 (2)	C7—H7	0.9300
O4—C11	1.203 (2)	C7—C8	1.371 (2)
O5—N1	1.222 (2)	C8—C9	1.442 (2)
O6—N1	1.218 (2)	C8—C11	1.457 (2)
N1—C1	1.467 (3)	C10—C12	1.505 (3)
N2—H2	0.8600	C10—C13	1.511 (3)
N2—C4	1.396 (2)	C12—H12B	0.9600
N2—C7	1.330 (2)	C12—H12C	0.9600
C1—C2	1.375 (3)	C12—H12A	0.9600
C1—C6	1.378 (3)	C13—H13B	0.9600
C2—H2A	0.9300	C13—H13C	0.9600
C2—C3	1.375 (2)	C13—H13A	0.9600
O1—C9—C8	117.28 (15)	C5—C4—N2	123.12 (16)
O1—C10—C12	109.17 (17)	C5—C4—C3	118.49 (16)
O1—C10—C13	105.94 (16)	C5—C6—C1	118.96 (19)
O2—C10—O1	110.53 (15)	C5—C6—H6	120.5
O2—C10—C12	109.99 (15)	C6—C1—N1	119.67 (19)
O2—C10—C13	106.34 (17)	C6—C5—C4	120.78 (17)
O2—C11—C8	115.76 (16)	C6—C5—H5	119.6
O3—C9—O1	117.76 (16)	C7—N2—H2	115.8
O3—C9—C8	124.94 (17)	C7—N2—C4	128.46 (15)
O4—C11—O2	118.24 (17)	C7—C8—C9	121.58 (16)
O4—C11—C8	125.91 (17)	C7—C8—C11	118.19 (16)
O5—N1—C1	118.4 (2)	C8—C7—H7	118.5
O6—N1—O5	123.2 (2)	C9—O1—C10	118.10 (13)
O6—N1—C1	118.38 (19)	C9—C8—C11	120.12 (16)
N2—C4—C3	118.39 (16)	C10—C12—H12B	109.5
N2—C7—H7	118.5	C10—C12—H12C	109.5
N2—C7—C8	123.03 (16)	C10—C12—H12A	109.5
C1—C2—H2A	120.7	C10—C13—H13B	109.5

C1—C2—C3	118.59 (17)	C10—C13—H13C	109.5
C1—C6—H6	120.5	C10—C13—H13A	109.5
C2—C1—N1	118.25 (18)	C11—O2—C10	118.74 (14)
C2—C1—C6	122.08 (18)	C12—C10—C13	114.77 (19)
C2—C3—Cl1	119.27 (14)	H12B—C12—H12C	109.5
C2—C3—C4	121.10 (17)	H12B—C12—H12A	109.5
C3—C2—H2A	120.7	H12C—C12—H12A	109.5
C4—N2—H2	115.8	H13B—C13—H13C	109.5
C4—C3—Cl1	119.63 (14)	H13B—C13—H13A	109.5
C4—C5—H5	119.6	H13C—C13—H13A	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.86	2.46	2.9328 (15)	115
N2—H2···O3	0.86	1.99	2.670 (2)	136