Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 6-amino-2-(chloromethyl)-5-cyano-4-*o*-tolyl-4*H*-pyran-3-carboxylate

S. Athimoolam,[a]* N. Savitha Devi,[b] S. Asath Bahadur,[a] R. Sayee Kannan[c] and S. Perumal[b]

[a]Department of Physics, Kalasalingam University, Anand Nagar, Krishnan Koil 626 190, India, [b]Department of Organic Chemistry, Madurai Kamaraj University, Madurai 625 021, India, and [c]Department of Chemistry, Thiagarajar College, Madurai 625 009, India
Correspondence e-mail: athi81s@yahoo.co.in

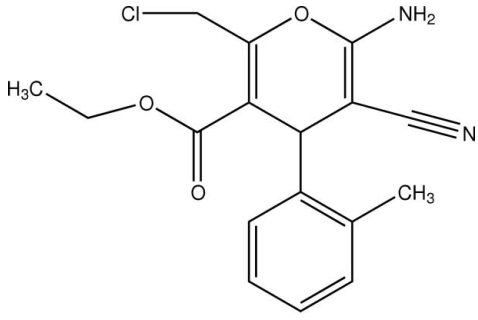
Received 2 November 2007; accepted 5 November 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.131; data-to-parameter ratio = 13.6.

In the title compound, $C_{17}H_{17}ClN_2O_3$, the six-membered pyran ring adopts a near-boat conformation. The crystal packing features two intramolecular C—H···O interactions and the crystal structure is stabilized by intermolecular N—H···O hydrogen bonds. These lead to two primary motifs, *viz.* $R_2^2(12)$ and $C(8)$. Combination of these primary motifs leads to a secondary $R_2^2(20)$ ring motif.

Related literature

For the biological importance of pyran derivatives, see: Marco *et al.* (1994); Morianka & Takahashi (1977); Miranda *et al.* (2006); Oliveira *et al.* (2007); Sun *et al.* (2005); Tietze (1983); Hatakeyama *et al.* (1988); Albert *et al.* (1997). For ring puckering analysis, see: Cremer & Pople (1975). For hydrogen-bonding interactons, see: Bernstein *et al.* (1995); Desiraju & Steiner (1999).



Experimental

Crystal data

$C_{17}H_{17}ClN_2O_3$
M_r = 332.78
Triclinic, $P\overline{1}$
a = 8.5734 (5) Å
b = 9.7735 (7) Å
c = 11.0781 (9) Å
α = 109.030 (11)°
β = 100.769 (15)°
γ = 103.813 (16)°
V = 815.96 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 293 (2) K
0.28 × 0.18 × 0.16 mm

Data collection

Enraf–Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.948, T_{max} = 0.965
3482 measured reflections
2858 independent reflections
1993 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.131
S = 1.06
2858 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···N12^{i}	0.86	2.23	3.078 (3)	169
N11—H11B···O2^{ii}	0.86	2.28	3.093 (3)	159
C7—H7···O2	0.98	2.44	2.785 (3)	100
C14—H14B···O1	0.97	2.31	2.927 (3)	121

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

SA and SAB sincerely thank the Vice Chancellor and Management of Kalasalingam University, Anand Nagar, Krishnan Koil, for their support and encouragement. RSK thanks the Principal and Management of Thiagarajar College.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2408).

References

Albert, A., Cano, F. H., Martin, N., Ramos, A., Rodriguez, M., Segara, J. L. & Seoane, C. (1997). *J. Chem. Soc. Perkin Trans. 1*, pp. 3401–3406.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2000). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg. Germany.
Hatakeyama, S., Ochi, N., Numata, H. & Takano, S. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1202–1204.
Marco, J. L., Martin, N., Grau, A. M., Seoane, C., Albert, A. & Cano, F. H. (1994). *Tetrahedron*, **50**, 3509–3528.
Miranda, P. O., Padron, J. M., Padron, J. I., Villar, J. & Martin, V. S. (2006). *ChemMedChem.* **3**, 323–329.

  doi:10.1107/S160053680705581X

Morianka, Y. & Takahashi, K. J. (1977). *Jpn Kokai.* **17**, 498–507.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Oliveira, A. M., Oliveira, C. A. M., Rodrigues, L. M., Raposo, M. M., Machado, A. E., Nascimento, M. S., Nazareth, N. & Pinto, M. (2007). *Chem. Biodivers.* **5**, 980–990.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Sun, C. L., Pang, R. F., Zhang, H. & Yang, M. (2005). *Bioorg. Med. Chem. Lett.* **3**, 3257–3262.
Tietze, L. F. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 828–841.

supplementary materials

Acta Cryst. (2007). E**63**, o4680-o4681 [**doi:10.1107/S160053680705581X**]

Ethyl 6-amino-2-(chloromethyl)-5-cyano-4-*o*-tolyl-4*H*-pyran-3-carboxylate

S. Athimoolam, N. S. Devi, S. A. Bahadur, R. S. Kannan and S. Perumal

Comment

Pyran derivatives occupy an important place in the realm of natural and synthetic organic chemistry because of their biological and pharmacological properties as antisterility (Morianka & Takahashi, 1977), anti-cancer agents (Miranda *et al.*, 2006), anti-tumor agents (Oliveira *et al.*, 2007) and anti-HIV agents (Sun *et al.*, 2005). Polyfunctionalized dihydropyran is a common structural unit in a number of natural products such as secoiridoid monoterpenes and biogenetically related indole alkaloids (Tietze, 1983; Hatakeyama *et al.*, 1988). Further the 4*H*-pyran ring can be transformed to pyridine systems related to pharmacologically important calcium antagonists of the DHP type (Marco *et al.*, 1994; Albert *et al.*, 1997).

In the title pyran derivative (I), Fig. 1, the near boat conformation of the 6-membered pyran ring is confirmed from the puckering analysis [q_2 = 0.203 (2) Å, θ_2 = 2.9 (7)°, q_3 = −0.039 (3) Å; Cremer & Pople, 1975]. The molecular structure features two weak intramolecular C—H···O interactions (Desiraju & Steiner, 1999) with the carboxylate O atoms (Table 1). $R_2^2(12)$ ring motifs form centrosymmetric hydrogen-bonded dimers (Fig. 2) that are linked through another N—H···O hydrogen bond propagating a C(8) chain motif along the *a* axis. A combination of these two primary interactions leads to a secondary $R_2^2(20)$ ring motif (Fig. 3).

Experimental

A mixture of ethyl 4-chloroacetoacetate (0.303 g m, 1.8 mmol) and 2-(2-methylbenzylidene)malononitrile (0.310 g m, 1.8 mmol) and sodium acetate (0.151 g m, 1.8 mmol) in ethanol were heated until the color of the solution turned brown. The reaction mixture was then stirred at room temperature for 12 h to give ethyl 6-amino-2-(chloromethyl)-5-cyano-4-*o*-tolyl-4*H*-pyran-3-carboxylate in 63% yield. The compound was recrystallized from methanol: ethyl acetate, (1:1).

Refinement

All the H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and N—H = 0.86 Å and U_{iso}(H) = 1.2–1.5 U_{eq} (parent atom).

Figures

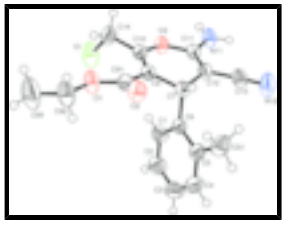


Fig. 1. The molecular structure of the title compound (I) with the numbering scheme for the atoms and 50% probability displacement ellipsoids.

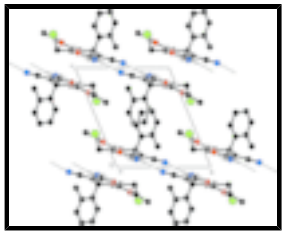


Fig. 2. Packing diagram of the molecules, viewed down the *a*-axis. H atoms not involved in the hydrogen bonds (dashed lines) are omitted for clarity.

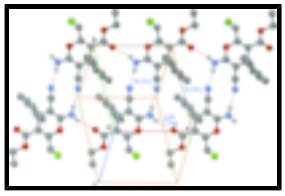


Fig. 3. A view of the ring and chain motifs formed through N—H···O hydrogen bonds (dotted lines).

Ethyl 6-amino-2-(chloromethyl)-5-cyano-4-*o*-tolyl-4*H*-pyran-3-carboxylate

Crystal data

$C_{17}H_{17}ClN_2O_3$	$Z = 2$
$M_r = 332.78$	$F_{000} = 348$
Triclinic, $P\overline{1}$	$D_x = 1.354$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.5734$ (5) Å	Cell parameters from 25 reflections
$b = 9.7735$ (7) Å	$\theta = 9.7$–13.3°
$c = 11.0781$ (9) Å	$\mu = 0.25$ mm^{-1}
$\alpha = 109.030$ (11)°	$T = 293$ (2) K
$\beta = 100.769$ (15)°	Needle, brown
$\gamma = 103.813$ (16)°	0.28 × 0.18 × 0.16 mm
$V = 815.96$ (17) Å^3	

Data collection

Enraf–Nonius MACH3 diffractometer	$R_{int} = 0.011$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.0^\circ$
Monochromator: graphite	$\theta_{min} = 2.0^\circ$
$T = 293(2)$ K	$h = -1 \rightarrow 10$
ω–2θ scans	$k = -11 \rightarrow 11$
Absorption correction: ψ scan (North et al., 1968)	$l = -13 \rightarrow 13$
$T_{min} = 0.948$, $T_{max} = 0.965$	3 standard reflections
3482 measured reflections	every 60 min
2858 independent reflections	intensity decay: none
1993 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.131$

$S = 1.06$

2858 reflections

210 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4918P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = <0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}

$\Delta\rho_{min} = -0.30$ e Å^{-3}

Extinction correction: none

Special details

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 $F^2 > 2$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}
Cl	0.32690 (12)	−0.08184 (11)	0.33517 (10)	0.0861 (3)
O1	−0.0894 (2)	−0.0308 (2)	0.2536 (2)	0.0585 (5)
O2	−0.1840 (2)	0.1044 (2)	0.14749 (19)	0.0526 (5)
O3	0.3657 (2)	0.10015 (19)	0.15335 (17)	0.0436 (4)
N11	0.5369 (3)	0.2408 (3)	0.0799 (2)	0.0498 (6)
H11A	0.5705	0.3136	0.0539	0.060*
H11B	0.5944	0.1803	0.0829	0.060*
N12	0.3448 (3)	0.5332 (3)	0.0489 (3)	0.0714 (8)
C1	0.2701 (3)	0.3942 (3)	0.4212 (3)	0.0473 (6)
H1	0.3153	0.3150	0.4115	0.057*
C2	0.3045 (4)	0.5061 (3)	0.5468 (3)	0.0578 (7)
H2	0.3713	0.5012	0.6208	0.069*
C3	0.2398 (4)	0.6239 (3)	0.5617 (3)	0.0632 (8)
H3	0.2641	0.7002	0.6456	0.076*
C4	0.1387 (4)	0.6291 (3)	0.4523 (3)	0.0582 (8)
H4	0.0940	0.7087	0.4636	0.070*
C5	0.1015 (3)	0.5174 (3)	0.3245 (3)	0.0450 (6)
C51	−0.0124 (4)	0.5265 (3)	0.2088 (3)	0.0626 (8)
H51A	−0.1101	0.4370	0.1695	0.094*
H51B	0.0457	0.5324	0.1436	0.094*
H51C	−0.0457	0.6159	0.2395	0.094*
C6	0.1692 (3)	0.3983 (3)	0.3095 (2)	0.0376 (5)

C7	0.1393 (3)	0.2751 (3)	0.1720 (2)	0.0368 (5)
H7	0.0424	0.2769	0.1103	0.044*
C9	0.0998 (3)	0.1183 (3)	0.1768 (2)	0.0366 (5)
C91	−0.0722 (3)	0.0626 (3)	0.1896 (2)	0.0403 (6)
C92	−0.2553 (4)	−0.0808 (4)	0.2728 (4)	0.0686 (9)
H92A	−0.2849	0.0075	0.3197	0.082*
H92B	−0.3392	−0.1384	0.1870	0.082*
C93	−0.2508 (6)	−0.1747 (5)	0.3488 (5)	0.1100 (16)
H93A	−0.3524	−0.1939	0.3743	0.165*
H93B	−0.1564	−0.1229	0.4272	0.165*
H93C	−0.2408	−0.2699	0.2956	0.165*
C10	0.2105 (3)	0.0427 (3)	0.1706 (2)	0.0393 (6)
C11	0.3952 (3)	0.2217 (3)	0.1158 (2)	0.0378 (5)
C12	0.2887 (3)	0.3040 (3)	0.1180 (2)	0.0379 (5)
C13	0.3230 (3)	0.4300 (3)	0.0790 (3)	0.0481 (6)
C14	0.1979 (4)	−0.1078 (3)	0.1787 (3)	0.0523 (7)
H14A	0.2330	−0.1691	0.1073	0.063*
H14B	0.0823	−0.1617	0.1682	0.063*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0893 (7)	0.1015 (7)	0.0988 (7)	0.0398 (5)	0.0248 (5)	0.0724 (6)
O1	0.0433 (11)	0.0735 (13)	0.0786 (14)	0.0176 (10)	0.0272 (10)	0.0500 (12)
O2	0.0401 (10)	0.0585 (11)	0.0681 (13)	0.0187 (9)	0.0212 (9)	0.0304 (10)
O3	0.0393 (10)	0.0483 (10)	0.0581 (11)	0.0199 (8)	0.0225 (8)	0.0304 (9)
N11	0.0414 (12)	0.0617 (14)	0.0665 (15)	0.0212 (11)	0.0273 (11)	0.0403 (12)
N12	0.0715 (18)	0.0817 (18)	0.103 (2)	0.0356 (15)	0.0477 (16)	0.0683 (18)
C1	0.0471 (15)	0.0520 (15)	0.0469 (15)	0.0192 (12)	0.0172 (12)	0.0199 (13)
C2	0.0573 (18)	0.0643 (19)	0.0426 (16)	0.0109 (15)	0.0094 (13)	0.0182 (14)
C3	0.071 (2)	0.0525 (17)	0.0544 (19)	0.0115 (15)	0.0267 (16)	0.0079 (14)
C4	0.0641 (19)	0.0433 (15)	0.072 (2)	0.0207 (14)	0.0331 (17)	0.0179 (15)
C5	0.0427 (14)	0.0408 (14)	0.0568 (16)	0.0129 (11)	0.0230 (12)	0.0213 (12)
C51	0.0647 (19)	0.0566 (17)	0.079 (2)	0.0323 (15)	0.0210 (16)	0.0329 (16)
C6	0.0343 (13)	0.0378 (12)	0.0443 (14)	0.0090 (10)	0.0182 (11)	0.0186 (11)
C7	0.0342 (13)	0.0407 (13)	0.0405 (13)	0.0142 (10)	0.0126 (10)	0.0197 (11)
C9	0.0360 (13)	0.0390 (13)	0.0361 (13)	0.0116 (10)	0.0124 (10)	0.0155 (10)
C91	0.0389 (14)	0.0387 (13)	0.0416 (14)	0.0102 (11)	0.0128 (11)	0.0145 (11)
C92	0.0465 (17)	0.086 (2)	0.091 (2)	0.0152 (16)	0.0331 (17)	0.053 (2)
C93	0.102 (3)	0.139 (4)	0.174 (5)	0.066 (3)	0.094 (3)	0.117 (4)
C10	0.0385 (13)	0.0408 (13)	0.0417 (14)	0.0116 (11)	0.0163 (11)	0.0180 (11)
C11	0.0350 (13)	0.0446 (13)	0.0377 (13)	0.0110 (11)	0.0127 (10)	0.0209 (11)
C12	0.0386 (13)	0.0420 (13)	0.0400 (13)	0.0146 (11)	0.0152 (11)	0.0211 (11)
C13	0.0447 (15)	0.0596 (16)	0.0561 (16)	0.0216 (13)	0.0259 (13)	0.0331 (14)
C14	0.0567 (17)	0.0465 (15)	0.0688 (19)	0.0231 (13)	0.0293 (15)	0.0303 (14)

Geometric parameters (Å, °)

Cl—C14	1.776 (3)	C51—H51A	0.9600

O1—C91	1.326 (3)	C51—H51B	0.9600
O1—C92	1.468 (3)	C51—H51C	0.9600
O2—C91	1.203 (3)	C6—C7	1.531 (3)
O3—C11	1.366 (3)	C7—C9	1.509 (3)
O3—C10	1.389 (3)	C7—C12	1.518 (3)
N11—C11	1.338 (3)	C7—H7	0.9800
N11—H11A	0.8600	C9—C10	1.334 (3)
N11—H11B	0.8600	C9—C91	1.495 (3)
N12—C13	1.147 (3)	C92—C93	1.435 (4)
C1—C2	1.385 (4)	C92—H92A	0.9700
C1—C6	1.389 (4)	C92—H92B	0.9700
C1—H1	0.9300	C93—H93A	0.9600
C2—C3	1.370 (4)	C93—H93B	0.9600
C2—H2	0.9300	C93—H93C	0.9600
C3—C4	1.375 (4)	C10—C14	1.483 (3)
C3—H3	0.9300	C11—C12	1.352 (3)
C4—C5	1.398 (4)	C12—C13	1.418 (3)
C4—H4	0.9300	C14—H14A	0.9700
C5—C6	1.397 (3)	C14—H14B	0.9700
C5—C51	1.501 (4)		
C91—O1—C92	115.9 (2)	C10—C9—C91	125.8 (2)
C11—O3—C10	119.47 (18)	C10—C9—C7	121.8 (2)
C11—N11—H11A	120.0	C91—C9—C7	112.4 (2)
C11—N11—H11B	120.0	O2—C91—O1	123.3 (2)
H11A—N11—H11B	120.0	O2—C91—C9	121.5 (2)
C2—C1—C6	121.1 (3)	O1—C91—C9	115.2 (2)
C2—C1—H1	119.4	C93—C92—O1	109.0 (3)
C6—C1—H1	119.4	C93—C92—H92A	109.9
C3—C2—C1	119.8 (3)	O1—C92—H92A	109.9
C3—C2—H2	120.1	C93—C92—H92B	109.9
C1—C2—H2	120.1	O1—C92—H92B	109.9
C2—C3—C4	119.9 (3)	H92A—C92—H92B	108.3
C2—C3—H3	120.1	C92—C93—H93A	109.5
C4—C3—H3	120.1	C92—C93—H93B	109.5
C3—C4—C5	121.5 (3)	H93A—C93—H93B	109.5
C3—C4—H4	119.2	C92—C93—H93C	109.5
C5—C4—H4	119.2	H93A—C93—H93C	109.5
C6—C5—C4	118.5 (3)	H93B—C93—H93C	109.5
C6—C5—C51	122.1 (2)	C9—C10—O3	122.2 (2)
C4—C5—C51	119.4 (2)	C9—C10—C14	129.7 (2)
C5—C51—H51A	109.5	O3—C10—C14	108.1 (2)
C5—C51—H51B	109.5	N11—C11—C12	128.7 (2)
H51A—C51—H51B	109.5	N11—C11—O3	110.2 (2)
C5—C51—H51C	109.5	C12—C11—O3	121.1 (2)
H51A—C51—H51C	109.5	C11—C12—C13	119.8 (2)
H51B—C51—H51C	109.5	C11—C12—C7	122.2 (2)
C1—C6—C5	119.2 (2)	C13—C12—C7	117.8 (2)
C1—C6—C7	119.3 (2)	N12—C13—C12	177.0 (3)
C5—C6—C7	121.4 (2)	C10—C14—Cl	109.9 (2)

C9—C7—C12	109.39 (19)	C10—C14—H14A	109.7
C9—C7—C6	110.96 (19)	Cl—C14—H14A	109.7
C12—C7—C6	111.99 (19)	C10—C14—H14B	109.7
C9—C7—H7	108.1	Cl—C14—H14B	109.7
C12—C7—H7	108.1	H14A—C14—H14B	108.2
C6—C7—H7	108.1		
C6—C1—C2—C3	−0.7 (4)	C7—C9—C91—O2	27.8 (3)
C1—C2—C3—C4	1.1 (4)	C10—C9—C91—O1	29.5 (4)
C2—C3—C4—C5	−0.9 (4)	C7—C9—C91—O1	−150.1 (2)
C3—C4—C5—C6	0.2 (4)	C91—O1—C92—C93	−177.3 (3)
C3—C4—C5—C51	178.7 (3)	C91—C9—C10—O3	177.4 (2)
C2—C1—C6—C5	0.0 (4)	C7—C9—C10—O3	−3.0 (4)
C2—C1—C6—C7	178.0 (2)	C91—C9—C10—C14	−2.1 (4)
C4—C5—C6—C1	0.3 (4)	C7—C9—C10—C14	177.5 (2)
C51—C5—C6—C1	−178.2 (2)	C11—O3—C10—C9	−13.0 (3)
C4—C5—C6—C7	−177.8 (2)	C11—O3—C10—C14	166.6 (2)
C51—C5—C6—C7	3.8 (4)	C10—O3—C11—N11	−168.1 (2)
C1—C6—C7—C9	45.2 (3)	C10—O3—C11—C12	11.8 (3)
C5—C6—C7—C9	−136.8 (2)	N11—C11—C12—C13	−0.3 (4)
C1—C6—C7—C12	−77.3 (3)	O3—C11—C12—C13	179.7 (2)
C5—C6—C7—C12	100.7 (3)	N11—C11—C12—C7	−175.0 (2)
C12—C7—C9—C10	17.4 (3)	O3—C11—C12—C7	5.0 (4)
C6—C7—C9—C10	−106.7 (3)	C9—C7—C12—C11	−18.5 (3)
C12—C7—C9—C91	−163.00 (19)	C6—C7—C12—C11	105.0 (3)
C6—C7—C9—C91	72.9 (2)	C9—C7—C12—C13	166.7 (2)
C92—O1—C91—O2	−0.7 (4)	C6—C7—C12—C13	−69.8 (3)
C92—O1—C91—C9	177.2 (2)	C9—C10—C14—Cl	−106.8 (3)
C10—C9—C91—O2	−152.5 (3)	O3—C10—C14—Cl	73.6 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11A···N12^{i}	0.86	2.23	3.078 (3)	169
N11—H11B···O2^{ii}	0.86	2.28	3.093 (3)	159
C7—H7···O2	0.98	2.44	2.785 (3)	100
C14—H14B···O1	0.97	2.31	2.927 (3)	121

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1, *y*, *z*.

Fig. 1

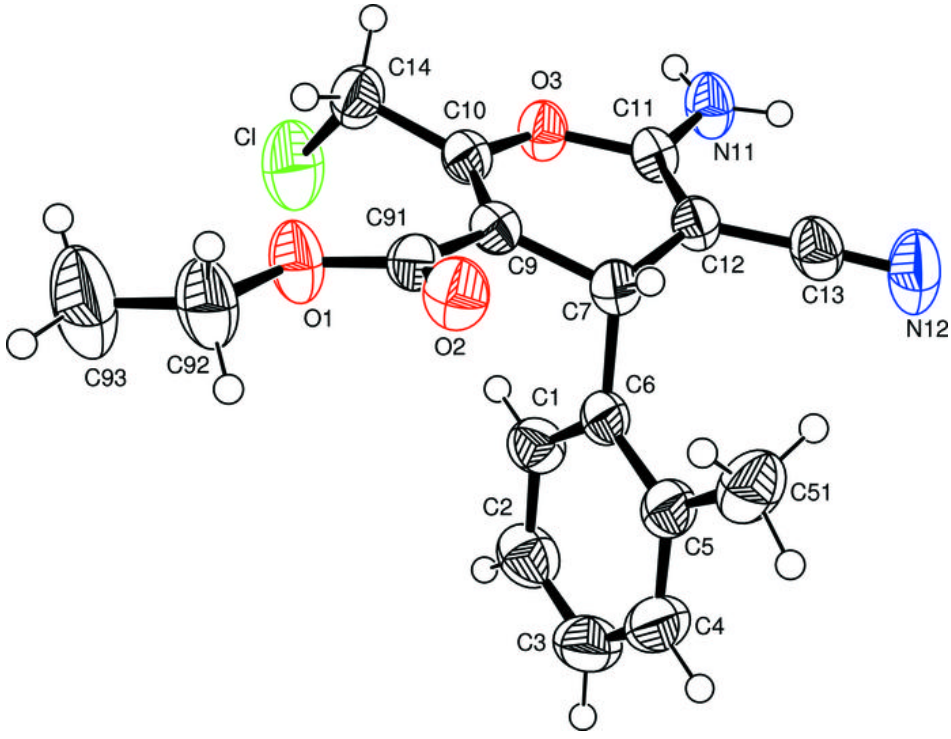

C14
O3
C10
C11
Cl
N11
C91
C9
C12
C13
N12
O1
O2
C7
C93
C92
C1
C6
C51
C2
C5
C4
C3

Fig. 2

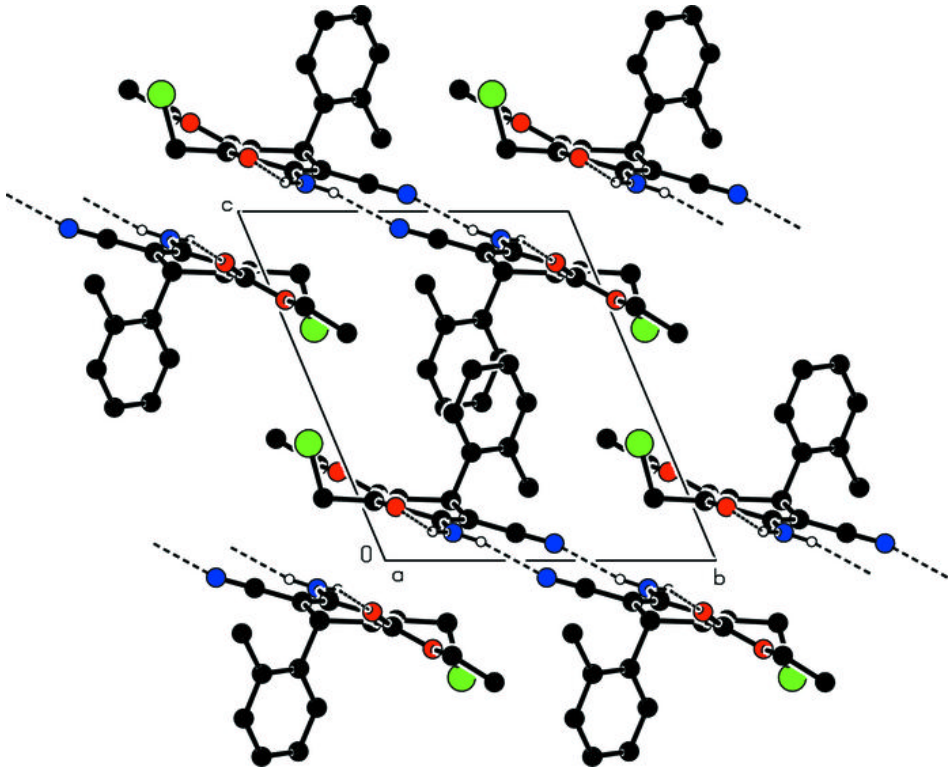


Fig. 3