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4-Chloro-3-fluoro-2-methylaniline–pyrrolidine-2,5-dione (1/1)

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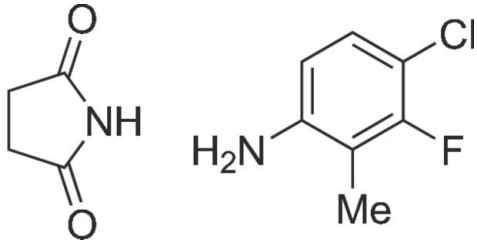
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 18.9.

Chlorination of 3-fluoro-2-methylaniline with *N*-chlorosuccinimide gave one major regioisomer whose structure was determined by X-ray crystallography. The product was found to have cocrystallized with succinimide, giving the title compound, $C_7H_7ClFN{\cdot}C_4H_5NO_2$. The crystal structure is stabilized by N—H···O hydrogen-bonding and π–π stacking interactions with a centroid–centroid distance of 3.4501 (8) Å.

Related literature

For related literature, see: Lazar *et al.* (2004); Marterer *et al.* (2003); Nickson & Roche-Dolson (1985); Shapiro *et al.* (2006); Tukada & Mazaki (1997); Zanka & Kubota (1999); Görbitz (1999).



Experimental

Crystal data

$C_7H_7ClFN{\cdot}C_4H_5NO_2$
M_r = 258.68
Triclinic, $P\overline{1}$
a = 7.3853 (2) Å
b = 7.4390 (2) Å
c = 11.5571 (4) Å
α = 73.1036 (13)°
β = 85.9336 (12)°
γ = 71.3703 (14)°
V = 575.53 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 120 K
0.75 × 0.44 × 0.41 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.47, T_{max} = 0.87
16689 measured reflections
2904 independent reflections
2610 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.087
S = 0.88
2904 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N12—H1···O16^{i}	0.85	2.11	2.945 (2)	168
N8—H9···O16^{i}	0.84	2.18	2.915 (2)	147
N8—H11···O17	0.88	2.17	3.030 (2)	166

Symmetry code: (i) $-x+2, -y, -z+1$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

We thank Dr Sarah F. Jenkinson, University of Oxford, for her assistance in the preparation of the manuscript.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2642).

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supplementary materials

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4-Chloro-3-fluoro-2-methylaniline-pyrrolidine-2,5-dione (1/1)

B. A. Mayes, P. McGarry, A. Moussa and D. J. Watkin

Comment

Chlorination of anilines with *N*-chlorosuccinimide (NCS) can provide access to poly-substituted aromatic compounds, useful as high-value synthetic intermediates (Lazar *et al.,* 2004; Marterer *et al.*, 2003; Nickson & Roche-Dolson, 1985; Shapiro *et al.*, 2006; Zanka & Kubota, 1999). In the present example, treatment of 3-fluoro-2-methylaniline with NCS in polar solvents (*e.g. N*,*N*-dimethylformamide) resulted in chlorination *para* to the NH_2 as the primary regioisomer in 10-fold excess relative to the undesired *ortho* isomer.

The sample was supplied in the form of large crystalline aggregates (4 mm across) coated with perfluoropolyether oil as a preservative. A large (0.8x0.8x0.4 mm) section was cut from the mass. The material did not have a strong cleavage - the crystals just fractured erratically. Because of the risk that further cutting might totally destroy the sample, an initial X-ray data set was measured from this large sample. The results confirmed the expected structure, but also showed a co-crystallized molecule of succinimide (Tukada & Mazaki, 1997).

At the end of the initial data collection, the sample was further subdivided into an irregular block approximately 0.41x0.44x0.75 mm. Prescans showed that the further cutting of the crystal had introduced fractures, but the sample was still amenable to analysis. Because of the degraded quality of the crystal, a data set with a target redundancy of 3 (as opposed to the usual 1) was collected. This highly redundant dataset would enable corrections to be made for the poor crystal quality.

Structure solution was slightly complicated because of the unexpected succinimide, but after that refinement and the location of all hydrogen atoms was normal. The two components are shown in Fig. 1. Fig. 2 shows the plane-to-plane alternate stacking of the components, with minimum inter-planar spacing of 3.37Å - presumable π - π stacking. The columns of molecules are interconnected by N-H···O hydrogen bonds which form discreet centrosymmetric 4-component clusters (Fig. 3).

Experimental

3-Fluoro-2-methylaniline (550 mg, 4.40 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) or 1-methyl-2-pyrrolidinone (NMP) (5 ml) and cooled to 0–5°C under argon. *N*-Chlorosuccinimide (586 mg, 4.39 mmol) was added and the mixture was allowed to warm to room temperature over 15 h (Fig. 4). Dilution with ethyl acetate, washing with water, drying (sodium sulfate), filtration and evaporation of the solvents gave a crude oil.

Crystals were grown from isopropyl ether by seeding and storing at 4°C for two weeks. The solvent was decanted and the crystals coated with 2 drops of FOMBLIN perfluoropolyether oil.

Additional methods of characterization were recorded: m.p. 75.5–76.0°C; ^{1}H (400 MHz, d3-MeCN): δ = 2.04 (3*H*, d, *J* 2.0 Hz, C*H*$_3$), 2.62 (4*H*, s, C*H*$_2$C*H*$_2$), 4.32 (2*H*, br-s, N*H*$_2$), 6.46 (1*H*, dd, *J* 8.6 Hz, *J* 0.8 Hz), 7.00 (1*H*, a-t, *J* 8.6 Hz), 8.83 (1*H*, br-s, N*H*). ^{13}C (100 MHz, d3-MeCN): δ = 9.12, 9.18 (*C*H$_3$), 30.26 (*C*H$_2$*C*H$_2$), 107.99, 108.19 (*C*-2), 111.16

(*C*-6), 111.34, 111.37 (*C*-4), 127.97, 127.98 (*C*-3), 147.76, 147.82 (*C*-5), 156.09, 158.47 (*C*-1), 179.33 (2 *xC*=O) (using crystallographic numbering).

Refinement

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.85) reflect the poor quality of the sample.

Difficulties in selecting an integration box suitable for all frames were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*, Otwinowski & Minor, 1997).

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 N—H to 0.86 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

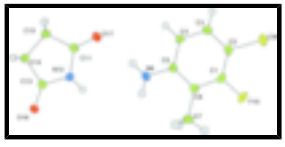

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

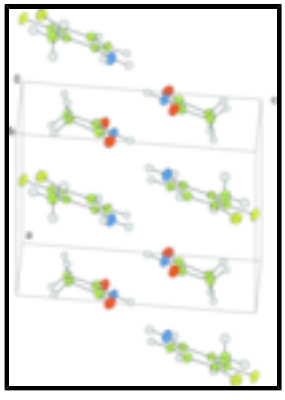

Fig. 2. Plane-to-plane stacking of alternate molecules parallel to the *a* axis.

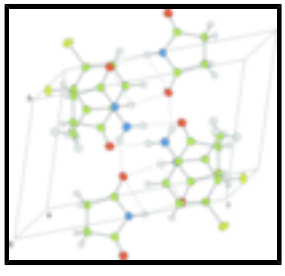

Fig. 3. The hydrogen bonds (dotted lines) in the π -π stacks.

Fig. 4. Synthetic scheme.

4-Chloro-3-fluoro-2-methylaniline–pyrrolidine-2,5-dione (1/1)

Crystal data

$C_7H_7ClFN·C_4H_5NO_2$	$Z = 2$
$M_r = 258.68$	$F_{000} = 268$
Triclinic, $P\overline{1}$	$D_x = 1.493$ Mg m^{-3}
$a = 7.3853$ (2) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 7.4390$ (2) Å	Cell parameters from 2870 reflections
$c = 11.5571$ (4) Å	$\theta = 5$–29º
$\alpha = 73.1036$ (13)º	$\mu = 0.34$ mm^{-1}
$\beta = 85.9336$ (12)º	$T = 120$ K
$\gamma = 71.3703$ (14)º	Plate, colourless
$V = 575.53$ (3) Å^3	0.75 × 0.44 × 0.41 mm

Data collection

Nonius KappaCCD diffractometer	2610 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
$T = 120$ K	$\theta_{max} = 28.7$º
ω scans	$\theta_{min} = 5.4$º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$h = -9\rightarrow9$
$T_{min} = 0.47$, $T_{max} = 0.87$	$k = -10\rightarrow9$
16689 measured reflections	$l = -15\rightarrow15$
2904 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.032$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.35P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.88$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
2904 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}
154 parameters	Extinction correction: None
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C11	0.94307 (16)	0.30918 (17)	0.66142 (11)	0.0207
N12	0.99166 (15)	0.16670 (15)	0.59934 (9)	0.0223
C13	1.10284 (16)	−0.01507 (17)	0.66627 (11)	0.0205
C14	1.14595 (16)	−0.00013 (17)	0.78815 (10)	0.0204
C15	1.04097 (16)	0.21516 (17)	0.78494 (11)	0.0211
O16	1.15499 (13)	−0.16202 (13)	0.62979 (8)	0.0275
O17	0.83954 (13)	0.47656 (13)	0.62086 (8)	0.0280
H141	1.2797	−0.0325	0.7987	0.0245*
H142	1.0987	−0.0916	0.8511	0.0240*
H151	1.1221	0.2859	0.7939	0.0258*
H152	0.9471	0.2271	0.8474	0.0263*
H1	0.9510	0.1824	0.5287	0.0265*
C1	0.34402 (16)	0.96277 (18)	0.14329 (10)	0.0201
C2	0.28607 (16)	1.11710 (17)	0.19551 (11)	0.0207
C3	0.34232 (16)	1.08204 (17)	0.31427 (11)	0.0217
C4	0.45586 (16)	0.89539 (17)	0.37673 (10)	0.0210
C5	0.51642 (16)	0.74038 (17)	0.32214 (10)	0.0188
C6	0.45694 (16)	0.77380 (17)	0.20237 (10)	0.0194
C7	0.51289 (19)	0.60873 (19)	0.14308 (12)	0.0269
N8	0.63360 (16)	0.55949 (16)	0.38422 (10)	0.0277
Cl9	0.14163 (4)	1.34735 (4)	0.11329 (3)	0.0293
F10	0.28435 (11)	0.99849 (12)	0.02806 (6)	0.0291
H31	0.3012	1.1851	0.3475	0.0277*
H41	0.4953	0.8705	0.4581	0.0257*
H71	0.6503	0.5518	0.1414	0.0420*
H72	0.4641	0.5027	0.1863	0.0416*
H73	0.4639	0.6536	0.0618	0.0429*
H9	0.6698	0.4664	0.3519	0.0324*
H11	0.6736	0.5392	0.4585	0.0317*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0199 (5)	0.0202 (5)	0.0235 (6)	−0.0059 (4)	0.0007 (4)	−0.0088 (4)
N12	0.0264 (5)	0.0201 (5)	0.0187 (5)	−0.0024 (4)	−0.0048 (4)	−0.0072 (4)
C13	0.0196 (5)	0.0201 (5)	0.0209 (5)	−0.0039 (4)	−0.0013 (4)	−0.0064 (4)
C14	0.0196 (5)	0.0216 (5)	0.0195 (5)	−0.0049 (4)	−0.0029 (4)	−0.0061 (4)
C15	0.0198 (5)	0.0232 (5)	0.0221 (6)	−0.0066 (4)	−0.0014 (4)	−0.0090 (4)
O16	0.0325 (5)	0.0212 (4)	0.0259 (5)	0.0005 (4)	−0.0056 (4)	−0.0108 (4)
O17	0.0302 (5)	0.0206 (4)	0.0305 (5)	−0.0012 (3)	−0.0058 (4)	−0.0090 (4)
C1	0.0196 (5)	0.0262 (6)	0.0156 (5)	−0.0089 (4)	−0.0015 (4)	−0.0051 (4)
C2	0.0180 (5)	0.0187 (5)	0.0228 (6)	−0.0049 (4)	−0.0023 (4)	−0.0023 (4)
C3	0.0217 (5)	0.0206 (5)	0.0237 (6)	−0.0051 (4)	0.0005 (4)	−0.0094 (4)
C4	0.0213 (5)	0.0228 (5)	0.0184 (5)	−0.0043 (4)	−0.0026 (4)	−0.0074 (4)

C5	0.0165 (5)	0.0190 (5)	0.0196 (5)	−0.0041 (4)	0.0003 (4)	−0.0050 (4)
C6	0.0181 (5)	0.0218 (5)	0.0205 (5)	−0.0081 (4)	0.0020 (4)	−0.0077 (4)
C7	0.0290 (6)	0.0277 (6)	0.0276 (6)	−0.0077 (5)	0.0010 (5)	−0.0144 (5)
N8	0.0317 (6)	0.0207 (5)	0.0241 (5)	0.0027 (4)	−0.0051 (4)	−0.0071 (4)
Cl9	0.02920 (17)	0.02088 (16)	0.03136 (17)	−0.00375 (11)	−0.00674 (12)	−0.00040 (11)
F10	0.0341 (4)	0.0346 (4)	0.0175 (3)	−0.0092 (3)	−0.0072 (3)	−0.0055 (3)

Geometric parameters (Å, °)

C11—N12	1.3890 (14)	C2—C3	1.3885 (17)
C11—C15	1.5141 (16)	C2—Cl9	1.7335 (12)
C11—O17	1.2075 (14)	C3—C4	1.3826 (16)
N12—C13	1.3689 (15)	C3—H31	0.913
N12—H1	0.852	C4—C5	1.4075 (16)
C13—C14	1.5082 (16)	C4—H41	0.952
C13—O16	1.2235 (14)	C5—C6	1.4096 (16)
C14—C15	1.5309 (16)	C5—N8	1.3629 (14)
C14—H141	0.947	C6—C7	1.5076 (16)
C14—H142	0.970	C7—H71	0.968
C15—H151	0.943	C7—H72	0.963
C15—H152	0.968	C7—H73	0.955
C1—C2	1.3848 (17)	N8—H9	0.842
C1—C6	1.3826 (16)	N8—H11	0.882
C1—F10	1.3569 (13)		
N12—C11—C15	107.80 (9)	C1—C2—C3	118.84 (11)
N12—C11—O17	124.27 (11)	C1—C2—Cl9	119.74 (9)
C15—C11—O17	127.93 (11)	C3—C2—Cl9	121.41 (9)
C11—N12—C13	113.60 (10)	C2—C3—C4	119.37 (11)
C11—N12—H1	125.7	C2—C3—H31	117.6
C13—N12—H1	120.5	C4—C3—H31	123.1
N12—C13—C14	108.74 (9)	C3—C4—C5	121.32 (11)
N12—C13—O16	123.80 (11)	C3—C4—H41	119.8
C14—C13—O16	127.46 (11)	C5—C4—H41	118.9
C13—C14—C15	104.82 (9)	C4—C5—C6	119.65 (11)
C13—C14—H141	109.5	C4—C5—N8	120.21 (11)
C15—C14—H141	111.9	C6—C5—N8	120.13 (10)
C13—C14—H142	109.2	C5—C6—C1	117.02 (10)
C15—C14—H142	111.7	C5—C6—C7	120.92 (11)
H141—C14—H142	109.5	C1—C6—C7	122.05 (11)
C14—C15—C11	104.97 (9)	C6—C7—H71	111.7
C14—C15—H151	114.0	C6—C7—H72	111.2
C11—C15—H151	109.0	H71—C7—H72	106.7
C14—C15—H152	112.8	C6—C7—H73	111.5
C11—C15—H152	109.9	H71—C7—H73	108.1
H151—C15—H152	106.2	H72—C7—H73	107.4
C2—C1—C6	123.78 (11)	C5—N8—H9	120.4
C2—C1—F10	118.07 (10)	C5—N8—H11	120.3
C6—C1—F10	118.14 (10)	H9—N8—H11	119.3

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H1···O16^{i}	0.85	2.11	2.945 (2)	168
N8—H9···O16^{i}	0.84	2.18	2.915 (2)	147
N8—H11···O17	0.88	2.17	3.030 (2)	166

Symmetry codes: (i) −*x*+2, −*y*, −*z*+1.

Fig. 1

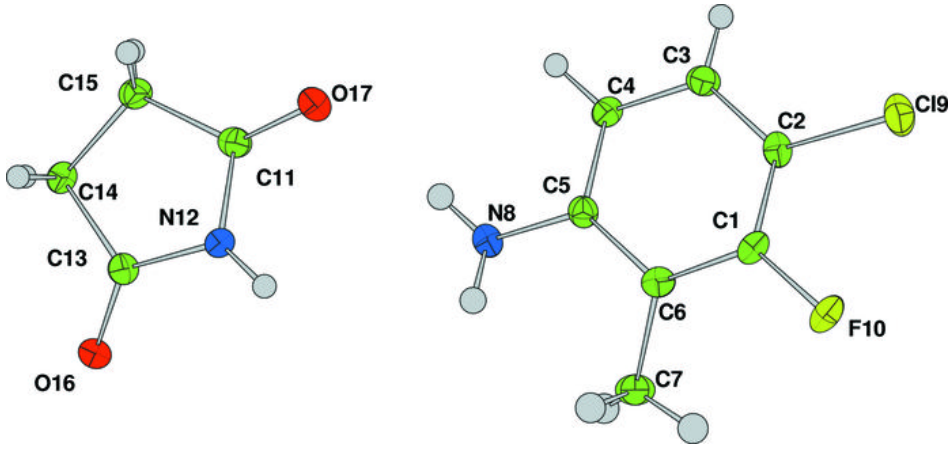

Fig. 2

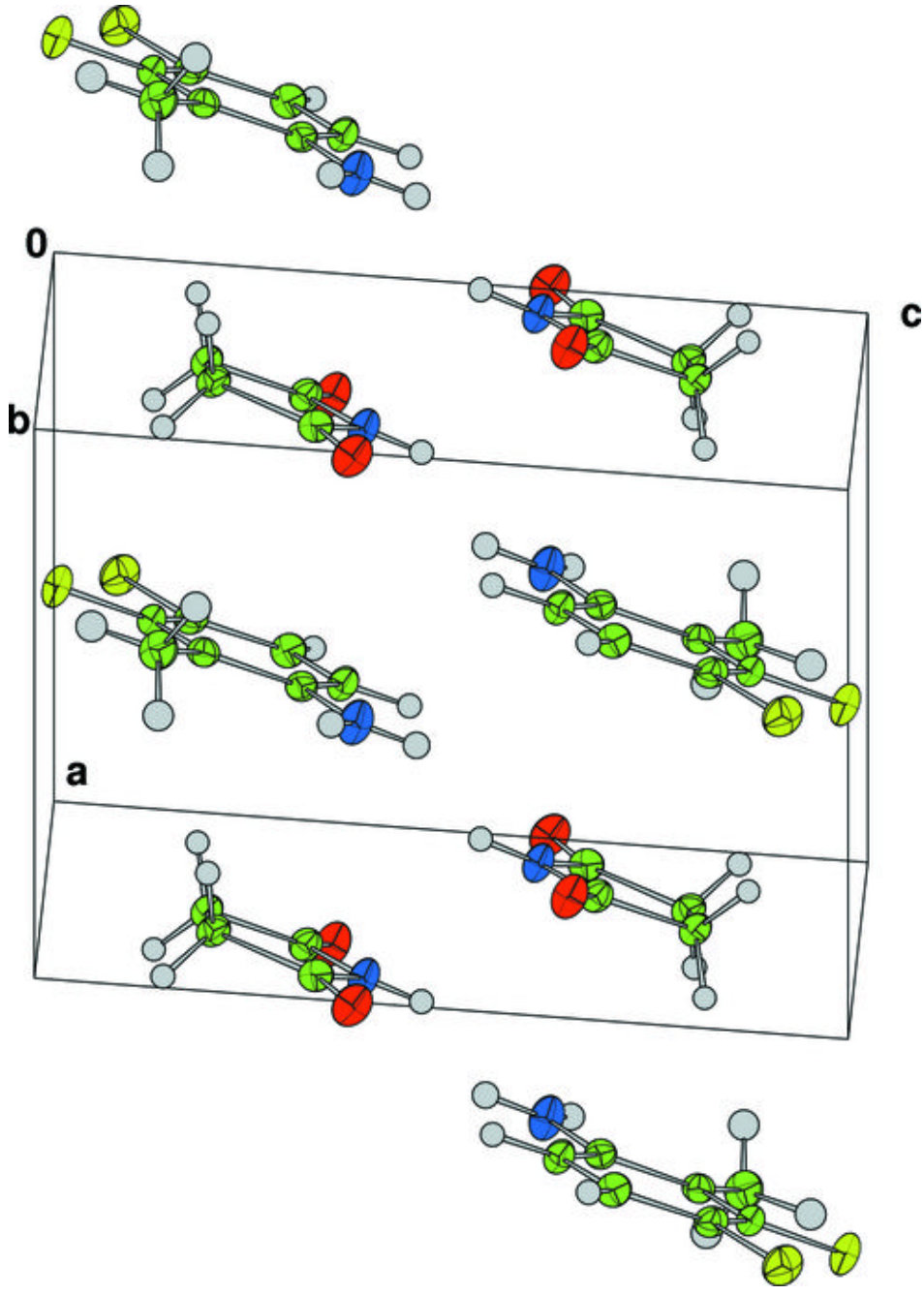

Fig. 3

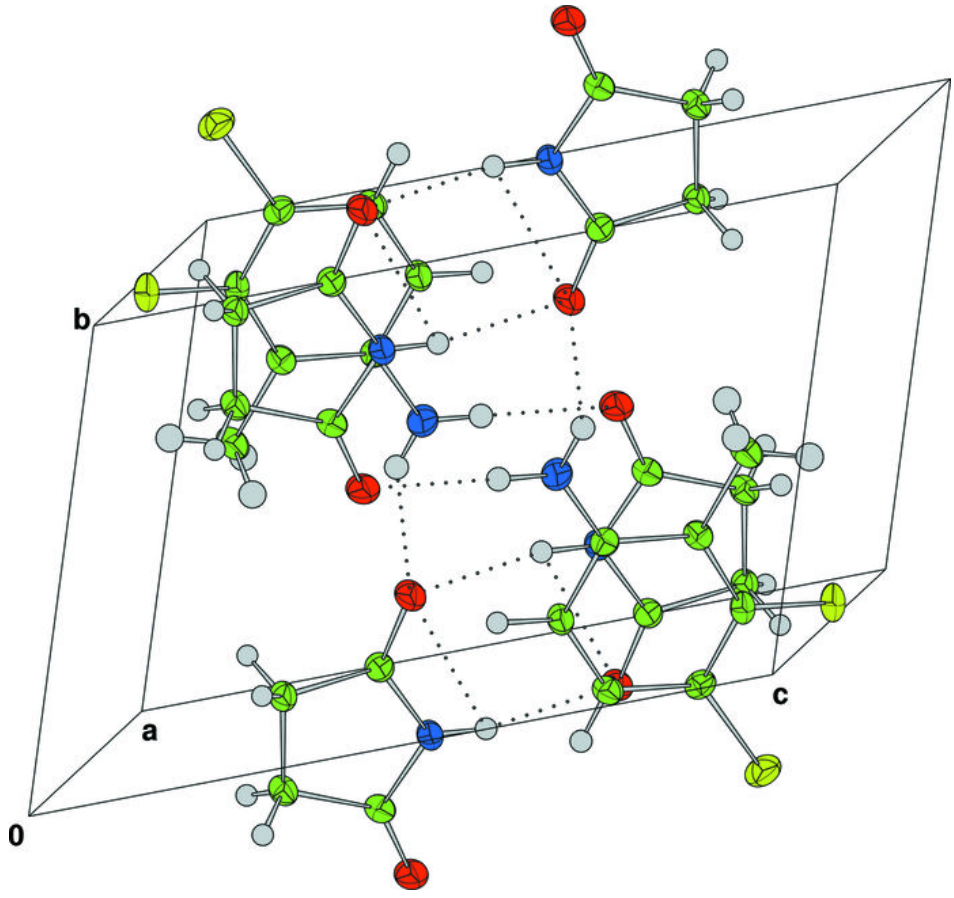

Fig. 4