

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1-(2,6-Difluorobenzoyl)-3-(2,3,5-trichlorophenyl)urea

Sheng-Jiao Yan,* Chao Huang, Yan-Mei Li, Yu-Yun Yan and Jun Lin*

School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resources, (Ministry of Education), Yunnan University, Kunming 650091, People's Republic of China

Correspondence e-mail: yanshengjiao@126.com

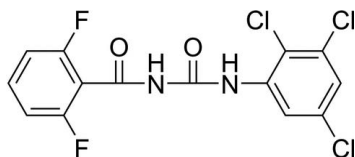
Received 1 May 2008; accepted 6 October 2008

Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.039; wR factor = 0.089; data-to-parameter ratio = 16.5.

The asymmetric unit of the title compound, $\text{C}_{14}\text{H}_7\text{Cl}_3\text{F}_2\text{N}_2\text{O}_2$, contains two unique molecules. The 2,3,5-trichlorophenyl ring is almost coplanar with the urea group in both molecules, whereas the 2,6-difluorophenyl ring is twisted from the urea plane by 54.83 (10)° in one molecule and 60.58 (10)° in the other. An intramolecular N—H—O hydrogen bond stabilizes the molecular conformation. The crystal packing is formed by intermolecular N—H—O hydrogen bonds and F···F interactions [2.841 (2) Å].

Related literature

For general background, see: Yan *et al.* (2003). For synthetic details, see: Lin *et al.* (2003, 2005).



Experimental

Crystal data

$\text{C}_{14}\text{H}_7\text{Cl}_3\text{F}_2\text{N}_2\text{O}_2$
 $M_r = 379.57$
 Monoclinic, $P2_1/c$

$a = 7.1669$ (4) Å
 $b = 22.8228$ (12) Å
 $c = 18.2885$ (10) Å

$\beta = 94.768$ (2)°
 $V = 2981.1$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation

$\mu = 0.65$ mm⁻¹
 $T = 113$ (2) K
 $0.24 \times 0.14 \times 0.12$ mm

Data collection

Rigaku Saturn diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2006)
 $T_{\min} = 0.860$, $T_{\max} = 0.927$

27779 measured reflections
 7091 independent reflections
 6011 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.089$
 $S = 1.07$
 7091 reflections
 431 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| $\text{N1}-\text{H1}\cdots\text{Cl1}$ | 0.89 (2) | 2.46 (2) | 2.9126 (15) | 111.8 (16) |
| $\text{N1}-\text{H1}\cdots\text{O2}$ | 0.89 (2) | 1.88 (2) | 2.641 (2) | 141.5 (19) |
| $\text{N2}-\text{H2}\cdots\text{O1}^{\text{i}}$ | 0.82 (2) | 2.00 (2) | 2.8205 (19) | 173 (2) |
| $\text{N3}-\text{H3}\cdots\text{Cl4}$ | 0.80 (2) | 2.43 (2) | 2.8944 (16) | 118.2 (19) |
| $\text{N3}-\text{H3}\cdots\text{O4}$ | 0.80 (2) | 1.99 (2) | 2.658 (2) | 140 (2) |
| $\text{N4}-\text{H4}\cdots\text{O3}^{\text{ii}}$ | 0.91 (2) | 1.93 (2) | 2.8378 (18) | 176 (2) |

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

Data collection: *CrystalClear* (Rigaku, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2006).

This project was supported by the 11th Five-Year Construction Item for Yunnan University Teachers (grant No. 0030-WX069051).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2065).

References

- Lin, J., Yan, S. J., Mao, D. S., Xu, R., Yang, L. J. & Liu, F. C. (2003). *Chin. Chem. Lett.* **14**, 1219–1222.
 Lin, J., Yan, S. J., Yang, L. J., Li, J. F. & Liu, F. C. (2005). *Chin. J. Org. Chem.* **25**, 304–307.
 Rigaku (2006). *CrystalClear* and *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Yan, S. J., Lin, J., Bi, F. C., Rang, L. J. & Cheng, Y. P. (2003). *J. Yunnan Univ.* **25**, 438–441.

supplementary materials

Acta Cryst. (2008). E64, o2102 [doi:10.1107/S1600536808032029]

1-(2,6-Difluorobenzoyl)-3-(2,3,5-trichlorophenyl)urea

S.-J. Yan, C. Huang, Y.-M. Li, Y.-Y. Yan and J. Lin

Comment

Derivatives of benzoylphenylureas (BPUs) are kind of insect growth regulators (IGRs), interferes the chitin synthesis in target pests, causing death or abortive development. BPUs possess high selectivity, low acute toxicity for mammals. At the time, the different groups on the phenyl that have different bioactivity. So research the configuration of the different compound is important to find more potent insecticide. The title compound (I) (Fig. 1), $C_{14}H_7Cl_3F_2N_2O_2$, which possesses high bioactivity to pests (Yan *et al.*, 2003).

The geometrical parameters for (I) (Table 1) show the conjugation present: the length of the C1=O1 and C=O2 double bond is greater than that of a normal C=O double bond. The lengths of the C1—N1, C1—N2, C8—N2 bonds are shorter than that of normal C—N single bonds. The 2,3,5-trichlorophenyl ring of the title compound is almost coplanar with the urea group, whereas the 2,6-difluorophenyl ring is twisted from the urea plane by 60.58 (10)°. An intramolecular N—H—O hydrogen bond stabilizes the molecular conformation. The crystal packing of the title compound formed by intermolecular N—H—O hydrogen bonds and F...F bond (Fig 2).

Experimental

A solution of 2,6-difluorobenzoyl isocyanate (II) (10 mmol, 1.0 equiv.) in 1,2-dichloroethane (10 ml) was added to a stirred solution of 2,3,5-trichloroaniline (III) (10 mmol, 1.0 equiv.) in dry 1,2-dichloroethane (20 ml) and stirred at room temperature for 24 hrs, the solvent was removed *in vacuo* and the residue was recrystallized with ethyl acetate to give desired compounds as white needle-crystals (I) in 93% yield (Lin *et al.*, 2003; Lin *et al.*, 2005). The desired product recrystallized from acetone (m.p. 517 K).

Refinement

In the absence of significant anomalous dispersion effects, Friedel pairs were merged; the absolute configuration was assigned on the basis of the known configuration of the starting material. All H atoms were placed in idealized positions and refined with riding constraints, with C—H distances in the range 0.93–0.96 Å and with $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$.

Figures

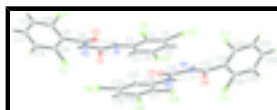


Fig. 1. View of (I) showing 30% displacement ellipsoids (arbitrary spheres for the H atoms).

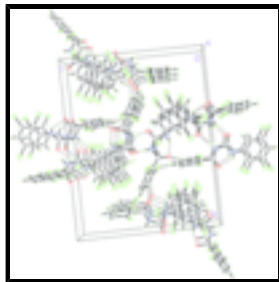


Fig. 2. The crystal packing of complex 1 showing the hydrogen bonds as broken lines. Symmetry code: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z$.



Fig. 3. The formation of the title compound.

1-(2,6-Difluorobenzoyl)-3-(2,3,5-trichlorophenyl)urea

Crystal data

$C_{14}H_7Cl_3F_2N_2O_2$

$M_r = 379.57$

Monoclinic, $P2_1/c$

$a = 7.1669$ (4) Å

$b = 22.8228$ (12) Å

$c = 18.2885$ (10) Å

$\beta = 94.768$ (2)°

$V = 2981.1$ (3) Å³

$Z = 8$

$F_{000} = 1520$

$D_x = 1.691$ Mg m⁻³

Melting point: 517 K

Mo $K\alpha$ radiation

$\lambda = 0.71070$ Å

Cell parameters from 6247 reflections

$\theta = 1.8$ – 27.9 °

$\mu = 0.65$ mm⁻¹

$T = 113$ (2) K

Prism, colourless

$0.24 \times 0.14 \times 0.12$ mm

Data collection

Rigaku Saturn
diffractometer

Radiation source: rotating anode

Monochromator: confocal

Detector resolution: 7.31 pixels mm⁻¹

$T = 113$ (2) K

ω and ϕ scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2006)

$T_{\min} = 0.860$, $T_{\max} = 0.927$

27779 measured reflections

7091 independent reflections

6011 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\text{max}} = 27.9$ °

$\theta_{\text{min}} = 1.8$ °

$h = -9 \rightarrow 9$

$k = -30 \rightarrow 30$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

| | |
|--|--|
| $wR(F^2) = 0.089$ | $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.1727P]$ |
| $S = 1.07$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 7091 reflections | $(\Delta/\sigma)_{\max} = 0.001$ |
| 431 parameters | $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$ |
| | 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|--------------|----------------------------------|
| C11 | 0.03364 (7) | 0.50654 (2) | 0.15961 (2) | 0.02733 (12) |
| C12 | -0.07937 (7) | 0.40202 (2) | 0.05408 (2) | 0.03038 (12) |
| C13 | -0.17311 (7) | 0.26475 (2) | 0.28607 (3) | 0.03149 (12) |
| C14 | 0.34943 (7) | 0.283841 (19) | 0.19434 (2) | 0.02671 (11) |
| C15 | 0.36147 (7) | 0.28306 (2) | 0.36548 (2) | 0.03282 (13) |
| C16 | 0.54168 (7) | 0.51085 (2) | 0.37218 (2) | 0.02918 (12) |
| F1 | -0.17544 (16) | 0.64246 (6) | 0.45899 (7) | 0.0423 (3) |
| F2 | 0.44718 (15) | 0.65048 (6) | 0.39926 (7) | 0.0414 (3) |
| F3 | 0.04346 (14) | 0.34365 (5) | -0.10568 (6) | 0.0303 (3) |
| F4 | 0.67828 (15) | 0.39222 (5) | -0.10684 (6) | 0.0327 (3) |
| O1 | -0.02709 (19) | 0.44667 (6) | 0.42993 (6) | 0.0291 (3) |
| O2 | 0.14058 (17) | 0.59069 (6) | 0.31730 (6) | 0.0248 (3) |
| O3 | 0.51390 (18) | 0.48843 (5) | 0.09749 (6) | 0.0247 (3) |
| O4 | 0.33939 (17) | 0.32720 (5) | 0.01436 (6) | 0.0240 (3) |
| N1 | 0.0186 (2) | 0.48145 (7) | 0.31516 (8) | 0.0214 (3) |
| N2 | 0.0531 (2) | 0.54179 (7) | 0.41771 (8) | 0.0225 (3) |
| N3 | 0.4215 (2) | 0.39641 (7) | 0.12945 (8) | 0.0202 (3) |
| N4 | 0.4259 (2) | 0.42336 (7) | 0.00736 (8) | 0.0201 (3) |
| C1 | 0.0123 (3) | 0.48592 (8) | 0.38878 (9) | 0.0221 (4) |
| C2 | -0.0276 (2) | 0.43225 (8) | 0.27132 (9) | 0.0197 (4) |
| C3 | -0.0277 (2) | 0.43974 (8) | 0.19488 (9) | 0.0212 (4) |
| C4 | -0.0753 (2) | 0.39311 (8) | 0.14825 (9) | 0.0225 (4) |
| C5 | -0.1203 (2) | 0.33913 (8) | 0.17552 (10) | 0.0246 (4) |
| H5 | -0.1524 | 0.3073 | 0.1434 | 0.029* |
| C6 | -0.1176 (2) | 0.33237 (8) | 0.25079 (10) | 0.0226 (4) |

supplementary materials

| | | | | |
|-----|-------------|-------------|---------------|------------|
| C7 | -0.0722 (2) | 0.37795 (8) | 0.29909 (9) | 0.0215 (4) |
| H7 | -0.0717 | 0.3721 | 0.3505 | 0.026* |
| C8 | 0.1103 (2) | 0.59011 (8) | 0.38219 (9) | 0.0205 (4) |
| C9 | 0.1360 (2) | 0.64407 (8) | 0.42805 (9) | 0.0207 (4) |
| C10 | -0.0058 (3) | 0.66965 (9) | 0.46427 (10) | 0.0270 (4) |
| C11 | 0.0158 (3) | 0.72142 (9) | 0.50213 (11) | 0.0331 (5) |
| H11 | -0.0859 | 0.7382 | 0.5250 | 0.040* |
| C12 | 0.1879 (3) | 0.74862 (9) | 0.50626 (10) | 0.0314 (5) |
| H12 | 0.2058 | 0.7840 | 0.5334 | 0.038* |
| C13 | 0.3350 (3) | 0.72521 (8) | 0.47147 (10) | 0.0291 (4) |
| H13 | 0.4537 | 0.7440 | 0.4742 | 0.035* |
| C14 | 0.3047 (3) | 0.67426 (8) | 0.43304 (10) | 0.0252 (4) |
| C15 | 0.4574 (2) | 0.43923 (8) | 0.08133 (9) | 0.0193 (4) |
| C16 | 0.4364 (2) | 0.39918 (8) | 0.20631 (9) | 0.0193 (4) |
| C17 | 0.4017 (2) | 0.34714 (8) | 0.24369 (9) | 0.0205 (4) |
| C18 | 0.4090 (3) | 0.34667 (8) | 0.31982 (9) | 0.0227 (4) |
| C19 | 0.4524 (2) | 0.39688 (8) | 0.36001 (9) | 0.0241 (4) |
| H19 | 0.4574 | 0.3966 | 0.4121 | 0.029* |
| C20 | 0.4882 (2) | 0.44752 (8) | 0.32218 (9) | 0.0219 (4) |
| C21 | 0.4809 (2) | 0.44985 (8) | 0.24629 (9) | 0.0208 (4) |
| H21 | 0.5058 | 0.4854 | 0.2220 | 0.025* |
| C22 | 0.3743 (2) | 0.37040 (7) | -0.02176 (9) | 0.0181 (4) |
| C23 | 0.3613 (2) | 0.36860 (7) | -0.10363 (9) | 0.0185 (4) |
| C24 | 0.1951 (3) | 0.35418 (8) | -0.14347 (9) | 0.0219 (4) |
| C25 | 0.1753 (3) | 0.35137 (8) | -0.21846 (10) | 0.0265 (4) |
| H25 | 0.0583 | 0.3416 | -0.2438 | 0.032* |
| C26 | 0.3300 (3) | 0.36319 (8) | -0.25635 (10) | 0.0290 (4) |
| H26 | 0.3189 | 0.3617 | -0.3084 | 0.035* |
| C27 | 0.5015 (3) | 0.37721 (8) | -0.21950 (10) | 0.0281 (4) |
| H27 | 0.6082 | 0.3848 | -0.2456 | 0.034* |
| C28 | 0.5121 (2) | 0.37969 (8) | -0.14440 (10) | 0.0224 (4) |
| H1 | 0.050 (3) | 0.5150 (9) | 0.2941 (11) | 0.033 (6)* |
| H2 | 0.053 (3) | 0.5433 (10) | 0.4626 (12) | 0.039 (6)* |
| H3 | 0.392 (3) | 0.3651 (9) | 0.1119 (12) | 0.036 (7)* |
| H4 | 0.441 (3) | 0.4529 (10) | -0.0251 (12) | 0.045 (6)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|---------------|--------------|---------------|
| C11 | 0.0356 (3) | 0.0278 (3) | 0.0190 (2) | -0.0018 (2) | 0.00479 (18) | -0.00021 (17) |
| C12 | 0.0346 (3) | 0.0393 (3) | 0.0171 (2) | 0.0015 (2) | 0.00166 (18) | -0.00678 (18) |
| C13 | 0.0359 (3) | 0.0224 (3) | 0.0360 (3) | -0.0003 (2) | 0.0023 (2) | -0.00089 (19) |
| C14 | 0.0352 (3) | 0.0200 (2) | 0.0249 (2) | -0.00355 (19) | 0.00249 (19) | 0.00437 (17) |
| C15 | 0.0422 (3) | 0.0311 (3) | 0.0256 (2) | -0.0054 (2) | 0.0058 (2) | 0.01259 (19) |
| C16 | 0.0362 (3) | 0.0271 (3) | 0.0243 (2) | 0.0022 (2) | 0.00324 (19) | -0.00380 (18) |
| F1 | 0.0232 (6) | 0.0534 (9) | 0.0519 (8) | -0.0052 (6) | 0.0122 (5) | -0.0179 (6) |
| F2 | 0.0237 (6) | 0.0504 (8) | 0.0518 (8) | -0.0071 (6) | 0.0141 (5) | -0.0213 (6) |
| F3 | 0.0211 (6) | 0.0405 (7) | 0.0298 (6) | -0.0052 (5) | 0.0058 (5) | 0.0026 (5) |

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| F4 | 0.0204 (6) | 0.0436 (7) | 0.0345 (6) | -0.0041 (5) | 0.0055 (5) | -0.0001 (5) |
| O1 | 0.0437 (8) | 0.0258 (7) | 0.0185 (6) | -0.0046 (6) | 0.0073 (6) | -0.0011 (5) |
| O2 | 0.0277 (7) | 0.0292 (7) | 0.0178 (6) | -0.0046 (6) | 0.0037 (5) | -0.0016 (5) |
| O3 | 0.0349 (8) | 0.0192 (7) | 0.0204 (6) | -0.0058 (6) | 0.0052 (5) | 0.0014 (5) |
| O4 | 0.0319 (7) | 0.0177 (7) | 0.0229 (6) | -0.0010 (5) | 0.0050 (5) | 0.0041 (5) |
| N1 | 0.0256 (9) | 0.0223 (9) | 0.0166 (7) | -0.0023 (7) | 0.0035 (6) | -0.0022 (6) |
| N2 | 0.0290 (9) | 0.0241 (9) | 0.0149 (7) | -0.0038 (7) | 0.0048 (6) | -0.0033 (6) |
| N3 | 0.0258 (8) | 0.0179 (8) | 0.0172 (7) | -0.0012 (7) | 0.0031 (6) | 0.0026 (6) |
| N4 | 0.0257 (8) | 0.0174 (8) | 0.0176 (7) | -0.0017 (6) | 0.0039 (6) | 0.0034 (6) |
| C1 | 0.0236 (10) | 0.0244 (10) | 0.0184 (8) | -0.0008 (8) | 0.0027 (7) | -0.0035 (7) |
| C2 | 0.0163 (9) | 0.0248 (10) | 0.0182 (8) | 0.0019 (7) | 0.0023 (7) | -0.0053 (7) |
| C3 | 0.0180 (9) | 0.0248 (10) | 0.0212 (8) | 0.0025 (7) | 0.0032 (7) | -0.0002 (7) |
| C4 | 0.0177 (9) | 0.0317 (11) | 0.0178 (8) | 0.0041 (8) | 0.0007 (7) | -0.0059 (7) |
| C5 | 0.0216 (10) | 0.0263 (10) | 0.0259 (9) | 0.0025 (8) | 0.0026 (7) | -0.0067 (7) |
| C6 | 0.0179 (9) | 0.0216 (10) | 0.0286 (9) | 0.0031 (7) | 0.0031 (7) | -0.0017 (7) |
| C7 | 0.0182 (9) | 0.0265 (10) | 0.0198 (8) | 0.0029 (7) | 0.0015 (7) | -0.0006 (7) |
| C8 | 0.0155 (9) | 0.0257 (10) | 0.0203 (8) | 0.0000 (7) | 0.0017 (7) | 0.0000 (7) |
| C9 | 0.0220 (9) | 0.0226 (10) | 0.0173 (8) | 0.0009 (7) | 0.0005 (7) | 0.0004 (7) |
| C10 | 0.0212 (10) | 0.0313 (11) | 0.0287 (10) | 0.0002 (8) | 0.0040 (8) | -0.0021 (8) |
| C11 | 0.0374 (12) | 0.0305 (12) | 0.0325 (11) | 0.0085 (9) | 0.0101 (9) | -0.0058 (8) |
| C12 | 0.0482 (13) | 0.0213 (10) | 0.0249 (9) | 0.0001 (9) | 0.0043 (9) | -0.0016 (8) |
| C13 | 0.0349 (12) | 0.0274 (11) | 0.0251 (9) | -0.0068 (9) | 0.0028 (8) | 0.0001 (8) |
| C14 | 0.0235 (10) | 0.0278 (11) | 0.0250 (9) | -0.0001 (8) | 0.0052 (7) | -0.0012 (7) |
| C15 | 0.0188 (9) | 0.0206 (10) | 0.0190 (8) | 0.0016 (7) | 0.0039 (7) | 0.0029 (7) |
| C16 | 0.0171 (9) | 0.0221 (9) | 0.0190 (8) | 0.0025 (7) | 0.0027 (7) | 0.0039 (7) |
| C17 | 0.0175 (9) | 0.0213 (10) | 0.0231 (9) | 0.0011 (7) | 0.0034 (7) | 0.0036 (7) |
| C18 | 0.0219 (9) | 0.0244 (10) | 0.0221 (9) | 0.0023 (8) | 0.0047 (7) | 0.0090 (7) |
| C19 | 0.0227 (10) | 0.0316 (11) | 0.0185 (8) | 0.0034 (8) | 0.0049 (7) | 0.0044 (7) |
| C20 | 0.0184 (9) | 0.0243 (10) | 0.0232 (9) | 0.0040 (7) | 0.0027 (7) | -0.0003 (7) |
| C21 | 0.0199 (9) | 0.0206 (9) | 0.0223 (9) | 0.0028 (7) | 0.0039 (7) | 0.0047 (7) |
| C22 | 0.0156 (9) | 0.0177 (9) | 0.0214 (8) | 0.0036 (7) | 0.0032 (7) | -0.0001 (7) |
| C23 | 0.0217 (9) | 0.0147 (9) | 0.0197 (8) | 0.0030 (7) | 0.0049 (7) | 0.0013 (6) |
| C24 | 0.0237 (10) | 0.0179 (9) | 0.0250 (9) | -0.0003 (7) | 0.0075 (7) | 0.0028 (7) |
| C25 | 0.0301 (11) | 0.0239 (10) | 0.0249 (9) | -0.0028 (8) | -0.0017 (8) | 0.0020 (7) |
| C26 | 0.0461 (13) | 0.0223 (10) | 0.0192 (9) | -0.0019 (9) | 0.0056 (8) | -0.0004 (7) |
| C27 | 0.0328 (11) | 0.0251 (11) | 0.0283 (10) | -0.0008 (8) | 0.0142 (8) | 0.0011 (8) |
| C28 | 0.0209 (9) | 0.0203 (10) | 0.0265 (9) | 0.0010 (7) | 0.0040 (7) | -0.0014 (7) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|---------|-----------|
| C11—C3 | 1.7265 (18) | C5—H5 | 0.9500 |
| C12—C4 | 1.7320 (18) | C6—C7 | 1.386 (2) |
| C13—C6 | 1.7317 (19) | C7—H7 | 0.9500 |
| C14—C17 | 1.7280 (18) | C8—C9 | 1.493 (2) |
| C15—C18 | 1.7228 (18) | C9—C10 | 1.387 (2) |
| C16—C20 | 1.7362 (19) | C9—C14 | 1.388 (3) |
| F1—C10 | 1.361 (2) | C10—C11 | 1.372 (3) |
| F2—C14 | 1.350 (2) | C11—C12 | 1.377 (3) |
| F3—C24 | 1.357 (2) | C11—H11 | 0.9500 |

supplementary materials

| | | | |
|------------|-------------|-------------|-------------|
| F4—C28 | 1.355 (2) | C12—C13 | 1.383 (3) |
| O1—C1 | 1.218 (2) | C12—H12 | 0.9500 |
| O2—C8 | 1.224 (2) | C13—C14 | 1.367 (3) |
| O3—C15 | 1.222 (2) | C13—H13 | 0.9500 |
| O4—C22 | 1.224 (2) | C16—C21 | 1.391 (2) |
| N1—C1 | 1.355 (2) | C16—C17 | 1.403 (2) |
| N1—C2 | 1.403 (2) | C17—C18 | 1.389 (2) |
| N1—H1 | 0.89 (2) | C18—C19 | 1.383 (3) |
| N2—C8 | 1.360 (2) | C19—C20 | 1.382 (2) |
| N2—C1 | 1.402 (2) | C19—H19 | 0.9500 |
| N2—H2 | 0.82 (2) | C20—C21 | 1.386 (2) |
| N3—C15 | 1.354 (2) | C21—H21 | 0.9500 |
| N3—C16 | 1.402 (2) | C22—C23 | 1.493 (2) |
| N3—H3 | 0.80 (2) | C23—C24 | 1.383 (2) |
| N4—C22 | 1.360 (2) | C23—C28 | 1.386 (2) |
| N4—C15 | 1.401 (2) | C24—C25 | 1.369 (2) |
| N4—H4 | 0.91 (2) | C25—C26 | 1.382 (3) |
| C2—C7 | 1.387 (2) | C25—H25 | 0.9500 |
| C2—C3 | 1.408 (2) | C26—C27 | 1.389 (3) |
| C3—C4 | 1.388 (2) | C26—H26 | 0.9500 |
| C4—C5 | 1.377 (3) | C27—C28 | 1.370 (2) |
| C5—C6 | 1.384 (2) | C27—H27 | 0.9500 |
| C1—N1—C2 | 127.03 (16) | C14—C13—C12 | 118.06 (19) |
| C1—N1—H1 | 113.2 (13) | C14—C13—H13 | 121.0 |
| C2—N1—H1 | 119.6 (13) | C12—C13—H13 | 121.0 |
| C8—N2—C1 | 128.23 (15) | F2—C14—C13 | 118.90 (17) |
| C8—N2—H2 | 117.9 (15) | F2—C14—C9 | 117.26 (16) |
| C1—N2—H2 | 113.4 (15) | C13—C14—C9 | 123.81 (18) |
| C15—N3—C16 | 128.03 (16) | O3—C15—N3 | 125.68 (16) |
| C15—N3—H3 | 116.0 (16) | O3—C15—N4 | 119.67 (15) |
| C16—N3—H3 | 115.9 (16) | N3—C15—N4 | 114.65 (15) |
| C22—N4—C15 | 128.67 (14) | C21—C16—N3 | 124.02 (15) |
| C22—N4—H4 | 116.5 (14) | C21—C16—C17 | 119.34 (16) |
| C15—N4—H4 | 114.8 (14) | N3—C16—C17 | 116.64 (15) |
| O1—C1—N1 | 125.96 (17) | C18—C17—C16 | 120.11 (16) |
| O1—C1—N2 | 119.17 (15) | C18—C17—C14 | 120.36 (14) |
| N1—C1—N2 | 114.85 (15) | C16—C17—C14 | 119.53 (13) |
| C7—C2—N1 | 123.82 (15) | C19—C18—C17 | 120.96 (16) |
| C7—C2—C3 | 119.40 (16) | C19—C18—C15 | 119.04 (13) |
| N1—C2—C3 | 116.79 (16) | C17—C18—C15 | 120.00 (14) |
| C4—C3—C2 | 119.77 (17) | C20—C19—C18 | 118.02 (16) |
| C4—C3—C11 | 120.30 (14) | C20—C19—H19 | 121.0 |
| C2—C3—C11 | 119.93 (14) | C18—C19—H19 | 121.0 |
| C5—C4—C3 | 121.06 (16) | C19—C20—C21 | 122.72 (17) |
| C5—C4—C12 | 118.68 (14) | C19—C20—C16 | 118.33 (13) |
| C3—C4—C12 | 120.25 (15) | C21—C20—C16 | 118.94 (14) |
| C4—C5—C6 | 118.41 (17) | C20—C21—C16 | 118.84 (16) |
| C4—C5—H5 | 120.8 | C20—C21—H21 | 120.6 |
| C6—C5—H5 | 120.8 | C16—C21—H21 | 120.6 |

| | | | |
|---------------|--------------|-----------------|--------------|
| C5—C6—C7 | 122.24 (17) | O4—C22—N4 | 124.46 (16) |
| C5—C6—C13 | 119.04 (14) | O4—C22—C23 | 121.38 (15) |
| C7—C6—C13 | 118.72 (14) | N4—C22—C23 | 114.16 (14) |
| C6—C7—C2 | 119.11 (16) | C24—C23—C28 | 115.82 (16) |
| C6—C7—H7 | 120.4 | C24—C23—C22 | 120.91 (15) |
| C2—C7—H7 | 120.4 | C28—C23—C22 | 123.25 (16) |
| O2—C8—N2 | 123.81 (17) | F3—C24—C25 | 118.75 (16) |
| O2—C8—C9 | 120.80 (16) | F3—C24—C23 | 117.71 (15) |
| N2—C8—C9 | 115.39 (15) | C25—C24—C23 | 123.53 (17) |
| C10—C9—C14 | 115.37 (17) | C24—C25—C26 | 118.19 (17) |
| C10—C9—C8 | 123.65 (16) | C24—C25—H25 | 120.9 |
| C14—C9—C8 | 120.86 (16) | C26—C25—H25 | 120.9 |
| F1—C10—C11 | 119.38 (17) | C25—C26—C27 | 121.07 (17) |
| F1—C10—C9 | 117.38 (17) | C25—C26—H26 | 119.5 |
| C11—C10—C9 | 123.19 (18) | C27—C26—H26 | 119.5 |
| C10—C11—C12 | 118.59 (19) | C28—C27—C26 | 117.96 (17) |
| C10—C11—H11 | 120.7 | C28—C27—H27 | 121.0 |
| C12—C11—H11 | 120.7 | C26—C27—H27 | 121.0 |
| C11—C12—C13 | 120.94 (19) | F4—C28—C27 | 119.34 (16) |
| C11—C12—H12 | 119.5 | F4—C28—C23 | 117.21 (15) |
| C13—C12—H12 | 119.5 | C27—C28—C23 | 123.43 (17) |
| C2—N1—C1—O1 | 3.5 (3) | C16—N3—C15—O3 | 1.6 (3) |
| C2—N1—C1—N2 | -175.52 (16) | C16—N3—C15—N4 | -178.88 (16) |
| C8—N2—C1—O1 | 175.84 (18) | C22—N4—C15—O3 | 175.83 (17) |
| C8—N2—C1—N1 | -5.1 (3) | C22—N4—C15—N3 | -3.8 (3) |
| C1—N1—C2—C7 | -6.0 (3) | C15—N3—C16—C21 | 4.5 (3) |
| C1—N1—C2—C3 | 173.97 (17) | C15—N3—C16—C17 | -176.16 (17) |
| C7—C2—C3—C4 | 1.1 (3) | C21—C16—C17—C18 | 1.0 (3) |
| N1—C2—C3—C4 | -178.90 (16) | N3—C16—C17—C18 | -178.33 (16) |
| C7—C2—C3—C11 | -178.25 (13) | C21—C16—C17—C14 | -179.16 (13) |
| N1—C2—C3—C11 | 1.8 (2) | N3—C16—C17—C14 | 1.5 (2) |
| C2—C3—C4—C5 | -0.9 (3) | C16—C17—C18—C19 | -0.8 (3) |
| C11—C3—C4—C5 | 178.44 (14) | C14—C17—C18—C19 | 179.40 (14) |
| C2—C3—C4—C12 | 179.03 (13) | C16—C17—C18—C15 | 178.62 (14) |
| C11—C3—C4—C12 | -1.7 (2) | C14—C17—C18—C15 | -1.2 (2) |
| C3—C4—C5—C6 | 0.2 (3) | C17—C18—C19—C20 | 0.0 (3) |
| C12—C4—C5—C6 | -179.71 (13) | C15—C18—C19—C20 | -179.39 (13) |
| C4—C5—C6—C7 | 0.3 (3) | C18—C19—C20—C21 | 0.5 (3) |
| C4—C5—C6—C13 | -179.82 (13) | C18—C19—C20—C16 | 179.69 (14) |
| C5—C6—C7—C2 | -0.1 (3) | C19—C20—C21—C16 | -0.3 (3) |
| C13—C6—C7—C2 | -179.98 (13) | C16—C20—C21—C16 | -179.44 (13) |
| N1—C2—C7—C6 | 179.38 (16) | N3—C16—C21—C20 | 178.79 (16) |
| C3—C2—C7—C6 | -0.6 (3) | C17—C16—C21—C20 | -0.5 (3) |
| C1—N2—C8—O2 | -2.4 (3) | C15—N4—C22—O4 | 2.9 (3) |
| C1—N2—C8—C9 | 177.94 (17) | C15—N4—C22—C23 | -177.49 (16) |
| O2—C8—C9—C10 | 121.2 (2) | O4—C22—C23—C24 | 58.7 (2) |
| N2—C8—C9—C10 | -59.1 (2) | N4—C22—C23—C24 | -120.91 (18) |
| O2—C8—C9—C14 | -54.5 (2) | O4—C22—C23—C28 | -119.8 (2) |
| N2—C8—C9—C14 | 125.14 (18) | N4—C22—C23—C28 | 60.5 (2) |

supplementary materials

| | | | |
|-----------------|--------------|-----------------|--------------|
| C14—C9—C10—F1 | 178.06 (16) | C28—C23—C24—F3 | -179.26 (15) |
| C8—C9—C10—F1 | 2.1 (3) | C22—C23—C24—F3 | 2.1 (2) |
| C14—C9—C10—C11 | 0.6 (3) | C28—C23—C24—C25 | -0.8 (3) |
| C8—C9—C10—C11 | -175.38 (18) | C22—C23—C24—C25 | -179.46 (17) |
| F1—C10—C11—C12 | -179.34 (17) | F3—C24—C25—C26 | 178.90 (16) |
| C9—C10—C11—C12 | -1.9 (3) | C23—C24—C25—C26 | 0.5 (3) |
| C10—C11—C12—C13 | 1.7 (3) | C24—C25—C26—C27 | 0.4 (3) |
| C11—C12—C13—C14 | -0.1 (3) | C25—C26—C27—C28 | -0.8 (3) |
| C12—C13—C14—F2 | -179.42 (17) | C26—C27—C28—F4 | 178.83 (16) |
| C12—C13—C14—C9 | -1.3 (3) | C26—C27—C28—C23 | 0.4 (3) |
| C10—C9—C14—F2 | 179.24 (16) | C24—C23—C28—F4 | -178.09 (15) |
| C8—C9—C14—F2 | -4.7 (3) | C22—C23—C28—F4 | 0.5 (3) |
| C10—C9—C14—C13 | 1.1 (3) | C24—C23—C28—C27 | 0.4 (3) |
| C8—C9—C14—C13 | 177.14 (17) | C22—C23—C28—C27 | 178.97 (17) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|----------|-------------|-------------|---------------|
| N1—H1 \cdots C11 | 0.89 (2) | 2.46 (2) | 2.9126 (15) | 111.8 (16) |
| N1—H1 \cdots O2 | 0.89 (2) | 1.88 (2) | 2.641 (2) | 141.5 (19) |
| N2—H2 \cdots O1 ⁱ | 0.82 (2) | 2.00 (2) | 2.8205 (19) | 173 (2) |
| N3—H3 \cdots C14 | 0.80 (2) | 2.43 (2) | 2.8944 (16) | 118.2 (19) |
| N3—H3 \cdots O4 | 0.80 (2) | 1.99 (2) | 2.658 (2) | 140 (2) |
| N4—H4 \cdots O3 ⁱⁱ | 0.91 (2) | 1.93 (2) | 2.8378 (18) | 176 (2) |

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

Fig. 1

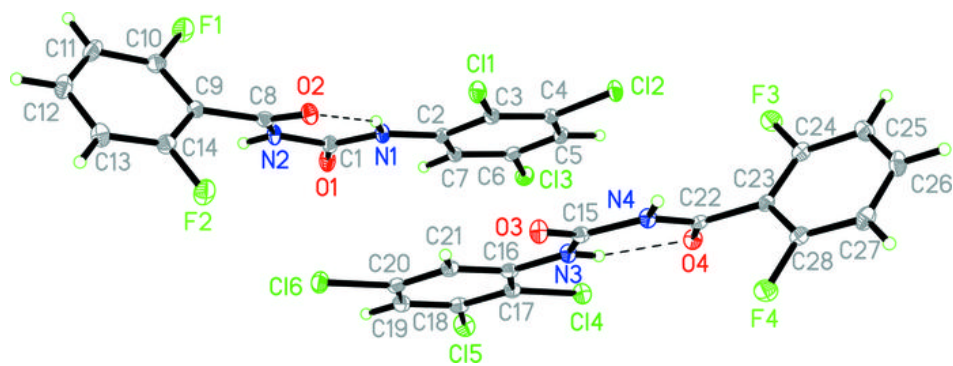


Fig. 2

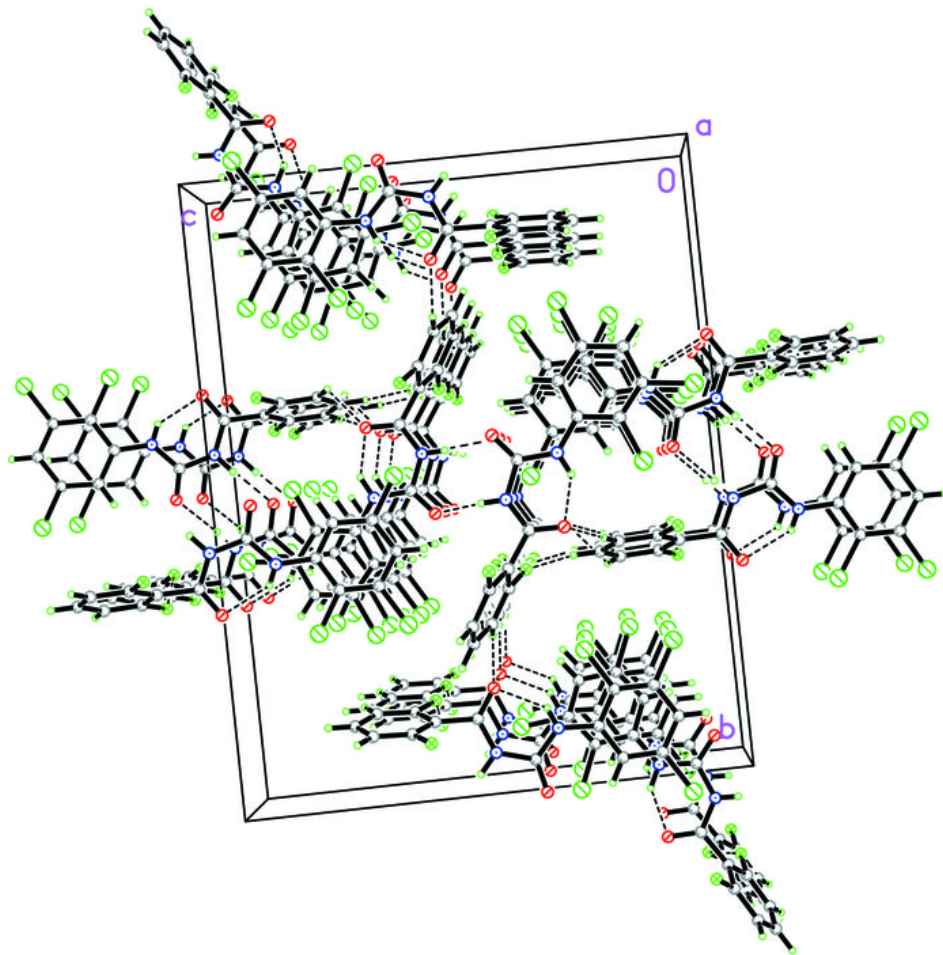


Fig. 3

