Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*Z*)-1,1-Dicyano-2-(4-fluorophenyl)-3-(1-hexylpyridin-1-ium-4-yl)prop-2-en-1-ide

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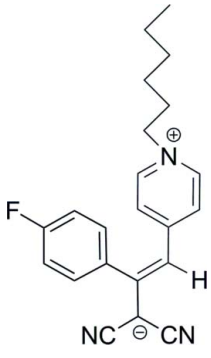
Received 18 November 2011; accepted 30 November 2011

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.080; data-to-parameter ratio = 14.4.

The title compound, $C_{22}H_{22}FN_3$, exists as a zwitterion with the negative charge on the dicyanomethanide group and the positive charge on the pyridinium N atom. The molecule adopts a Z conformation about the central C=C bond. The dihedral angle between the pyridinium and benzene rings is 65.65 (5)°. Weak C—H···N hydrogen bonding is present in the crystal structure.

Related literature

For details of zwitterionic chromophores and their applications, see: Hao (2011); Hao *et al.* (2011). For related structures, see: Metzger & Heimer (1984); Bell *et al.* (2002); Cole *et al.* (1997); Szablewski *et al.* (1997); Xiong *et al.*(2008). For the synthesis, see: Hao (2011). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{22}H_{22}FN_3$
M_r = 347.43
Monoclinic, $P2_1/c$
a = 10.485 (3) Å
b = 8.809 (2) Å
c = 21.313 (5) Å
β = 100.628 (4)°
V = 1934.7 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 295 K
0.24 × 0.21 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.982, T_{max} = 0.986
9762 measured reflections
3406 independent reflections
2154 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.080
S = 1.01
3406 reflections
237 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···N2^{i}	0.93	2.61	3.535 (3)	175
C16—H16A···N1^{ii}	0.93	2.51	3.354 (3)	151

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We acknowledge financial support for research from the Natural Sciences and Engineering Research Council of Canada, and NSFC grant No. 21110402016.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5392).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bell, N. A., Crouch, D. J., Simmonds, D. J., Goeta, A. E., Gelbrich, T. & Hursthouse, M. B. (2002). *J. Mater. Chem.* **12**, 1274–1279.
Cole, J. C., Cole, J. M., Cross, G. H., Farsari, M., Howard, J. A. K. & Szablewski, M. (1997). *Acta Cryst.* B**53**, 812–821.
Hao, W.-H. (2011). PhD thesis, Carleton University, Canada.
Hao, W.-H., McBride, A., McBride, S., Gao, J.-P. & Wang, Z.-Y. (2011). *J. Mater. Chem.* **21**, 1040–1048.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Metzger, R. M. & Heimer, N. E. (1984). *Mol. Cryst. Liq. Cryst.* **107**, 133–149.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalClear*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Szablewski, M., Thomas, P. R., Thornton, A., Bloor, D., Cross, G. H., Cole, J. M., Howard, J. A. K., Malagoli, M., Meyers, F., Bredas, J.-L., Wenseleers, W. & Goovaerts, E. (1997). *J. Am. Chem. Soc.* **119**, 3144–3154.
Xiong, Y., Tang, H., Zhang, J., Wang, Z.-Y., Campo, J., Wenseleers, W. & Goovaerts, E. (2008). *Chem. Mater.* **20**, 7465–7473.

supplementary materials

Acta Cryst. (2012). E**68**, o82 [**doi:10.1107/S160053681105166X**]

(*Z*)-1,1-Dicyano-2-(4-fluorophenyl)-3-(1-hexylpyridin-1-ium-4-yl)prop-2-en-1-ide

W.-H. Hao, C. Wang, G. Qian and Z.-Y. Wang

Comment

Structure determination of the title compound (I), $C_{22}H_{22}FN_3$ (Fig. 1), was performed as a part of a project in our laboratory on the synthesis of new series of D^+-π-A^- zwitterionic chromophores for electro-optic and near infrared chemosensor applications (Hao, 2011; Hao *et al.*, 2011).

The title compound (I) crystallizes as a zwitterion in which the negative charge on the dicyanomethanide (–$C(CN)_2$) group and the positive charge on the N atom in the pyridinium ring. It presents a Z configuration of the central C7═C11 double bond with the torsion angle C12—C11—C7—C8 being -168.25 (17) °.

The bond length between C7 and C11 (1.3837 (19) Å) is similar to the value observed in other zwitterionic compounds (Metzger & Heimer, 1984; Bell *et al.*, 2002), which clearly indicates the double bond π-bridge separating the pyridinium and dicyanomethanide groups. A significant displacement of electron density (or charge transfer)from the pyridinium ring (donor) to the –$C(CN)_2$ group (acceptor) was confirmed, corresponding to a large contribution of the zwitterionic resonance structure in compound (I).

The bond lengths between C7 and C8 (1.4078 (20) Å), C7 and C11 (1.3837 (19) Å) suggest electron delocalization among the three carbon atoms. However, more single bond characteristic is observed between C7 and C8;also evident from the observed two C—CN bonds (1.4111 (22) Å and 1.4201 (23) Å) in compound (I) *versus* 1.427 Å in typical 7,7,8,8-tetracyanoquino-dimethanes(TCNQs), indicating substantial negative charge localization within the –$C(CN)_2$ group, and elongated CN (1.1514 (20) Å and 1.1472 (20) Å) bond compared to that in typical TCNQs (1.144 Å) (Allen *et al.*, 1987) indicating a result of charge resonant stabilization *via* the two CN groups.

Although the bond lengths in the conjugated bridge and acceptor part clearly demonstrated a zwitterionic molecular structure of compound (I), the bond length of the pyridinium ring is quinoidal rather than aromatic. The C13—C14 and C15—C16 bonds (with bond lengths of 1.3516 (20) Å, 1.3491 (21) Å) are shorter than the C12—C13 and C12—C15 bonds (1.4088 (21) Å and 1.4125 (20) Å). Similar phenomena have also been reported for several TCNQ and 7,8-di(alkoxycarbonyl)-7,8- dicyanoquinodimethane zwitterionic adducts (Cole *et al.*, 1997; Szablewski *et al.*, 1997; Xiong *et al.*, 2008). Therefore, the best description of the ground state structure of compound (I) is the combination of the two limiting forms (Fig. 3), zwitterionic and neutral forms with predominantly zwitterionic structure.

As shown in Fig.2, two types of weak intermolecular C–H..N hydrogen bonds connect adjacent molecules, forming a 2-D layer structure in the *bc* plane with the bond lengths and angles being 3.354 (3) Å, 150.77 (1) ° (C16—H16A···N1) and 3.535 (2) Å, 174.79 (1) ° (C3—H3A···N2).

Experimental

Under anhydrous and oxygen-free conditions, to a 50 ml round-bottomed flask malononitrile (0.50 g, 7.4 mmol), sodium hydride (0.30 g, 60%, 7.5 mmol) and 2-(4-fluorophenyl)-3-pyridine-4-yl-acrylonitrile bromide salt (Hao, 2011) (1.0 g, 2.6 mmol) in 20 ml of THF were added at 0°C. After 30 min, the insoluble inorganic salt was removed by filtration, and the filtrate solution was concentrated under reduced pressure. The residue was purified by column chromatography (flash, mixture of acetone and hexane with the ratio 1:1) to produce (I) (0.56 g, 63% yield). Orange-red crystals were obtained from a hexane/acetone solution of (I) by slow evaporation at room temperature.

Refinement

The H atoms attached to the carbon atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, and were refined in the riding-model approximation with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the others,

Figures

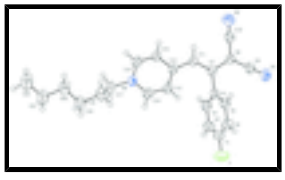


Fig. 1. The Molecular structure of compound (I) with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

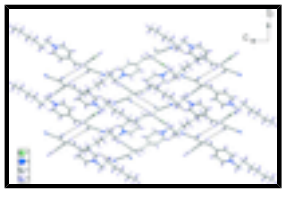


Fig. 2. Partial packing view showing the 2-D layer structure of compound (I) through two types of weak intermolecular C–H..N hydrogen bonds. Hydrogen bonds are shown by dashed lines.

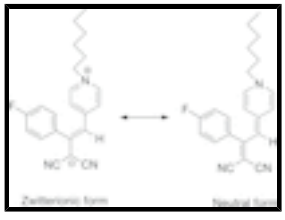


Fig. 3. Resonance structures of the title compound.

(*Z*)-1,1-Dicyano-2-(4-fluorophenyl)-3-(1-hexylpyridin-1-ium-4- yl)prop-2-en-1-ide

Crystal data

$C_{22}H_{22}FN_3$	$F(000)$ = 736
M_r = 347.43	D_x = 1.193 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 7543 reflections
a = 10.485 (3) Å	θ = 2.0–25.0°
b = 8.809 (2) Å	μ = 0.08 mm^{-1}
c = 21.313 (5) Å	T = 295 K

β = 100.628 (4)°	Prism, red
V = 1934.7 (8) Å^3	0.24 × 0.21 × 0.18 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID diffractometer	3406 independent reflections
Radiation source: fine-focus sealed tube	2154 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.046
Detector resolution: 10.000 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 1.9°
ω scans	h = −12→9
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	k = −10→10
T_{min} = 0.982, T_{max} = 0.986	l = −24→25
9762 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.043	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.080	H-atom parameters constrained
S = 1.01	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3406 reflections	$(\Delta/\sigma)_{max} < 0.001$
237 parameters	$\Delta\rho_{max}$ = 0.13 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Special details

Experimental. Melting point: 167 °C; UV-Vis: λ_{max} = 486 nm (DMF); FTIR (KBr, cm^{-1}): 2192, 1640, 1571, 1450; ^{1}H NMR (400 MHz, $(CD_3)_2SO$): (δ p.p.m.): 7.81 (2*H*, d, J = 7.1 Hz), 7.36 (2*H*, d, J = 8.7 Hz), 7.32 (2*H*, d, J = 8.7 Hz), 6.34 (2*H*, d, J = 7.1 Hz), 5.88 (1*H*, s), 3.92 (2*H*, t), 1.22 (6*H*, m), 0.83 (3*H*, t); ^{13} C NMR (100 MHz, $(CD_3)_2SO$: (δ p.p.m.): 161.2, 151.4, 139.8, 133.7, 130.0, 129.9, 119.8, 119.2, 118.2, 116.6, 116.4, 101.7, 56.7, 30.4,29.8, 24.9, 21.8, 13.7; TOF HRMS (ESI, DMF/Acetonitrile 1:1, m/*z*): Calculated value: 347.1798 $[M]^+$. Found: 348.1776 $[M + H]^+$, 370.1608 $[M + Na]^+$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
F	0.00950 (11)	0.32278 (14)	0.14713 (6)	0.0895 (4)
N1	0.52466 (16)	0.0019 (2)	0.21926 (7)	0.0776 (6)
N2	0.79360 (16)	0.0489 (2)	0.08676 (7)	0.0706 (5)
N3	0.31701 (13)	0.49453 (16)	−0.14317 (6)	0.0446 (4)
C1	0.12274 (18)	0.2874 (2)	0.12778 (9)	0.0548 (5)

C2	0.11792 (17)	0.1996 (2)	0.07511 (9)	0.0544 (5)
H2A	0.0392	0.1629	0.0530	0.065*
C3	0.23295 (17)	0.16598 (19)	0.05513 (8)	0.0472 (5)
H3A	0.2314	0.1067	0.0189	0.057*
C4	0.35090 (15)	0.21967 (18)	0.08855 (7)	0.0384 (4)
C5	0.34999 (16)	0.30647 (19)	0.14272 (8)	0.0457 (5)
H5A	0.4282	0.3411	0.1662	0.055*
C6	0.23523 (19)	0.3429 (2)	0.16267 (8)	0.0546 (5)
H6A	0.2349	0.4029	0.1985	0.065*
C7	0.47440 (15)	0.17940 (18)	0.06776 (7)	0.0384 (4)
C8	0.56746 (16)	0.10162 (19)	0.11230 (7)	0.0416 (4)
C9	0.54269 (17)	0.0483 (2)	0.17131 (9)	0.0507 (5)
C10	0.6924 (2)	0.0696 (2)	0.09897 (8)	0.0483 (5)
C11	0.49704 (15)	0.21053 (18)	0.00714 (7)	0.0429 (4)
H11A	0.5680	0.1601	−0.0035	0.051*
C12	0.43029 (15)	0.30640 (18)	−0.04143 (7)	0.0394 (4)
C13	0.33424 (16)	0.4152 (2)	−0.03586 (8)	0.0474 (5)
H13A	0.3067	0.4261	0.0030	0.057*
C14	0.28129 (16)	0.5040 (2)	−0.08563 (8)	0.0487 (5)
H14A	0.2180	0.5740	−0.0800	0.058*
C15	0.46572 (16)	0.30234 (19)	−0.10225 (8)	0.0474 (5)
H15A	0.5303	0.2353	−0.1091	0.057*
C16	0.40928 (17)	0.3923 (2)	−0.15072 (8)	0.0503 (5)
H16A	0.4343	0.3838	−0.1902	0.060*
C17	0.25548 (16)	0.5900 (2)	−0.19749 (8)	0.0493 (5)
H17A	0.3214	0.6252	−0.2206	0.059*
H17B	0.2167	0.6784	−0.1814	0.059*
C18	0.15272 (17)	0.5044 (2)	−0.24250 (8)	0.0600 (5)
H18A	0.0928	0.4587	−0.2183	0.072*
H18B	0.1935	0.4231	−0.2623	0.072*
C19	0.07691 (18)	0.6055 (2)	−0.29453 (8)	0.0680 (6)
H19A	0.0074	0.5459	−0.3192	0.082*
H19B	0.0372	0.6869	−0.2743	0.082*
C20	0.15573 (18)	0.6746 (2)	−0.33983 (8)	0.0630 (6)
H20A	0.2031	0.5948	−0.3569	0.076*
H20B	0.2187	0.7443	−0.3164	0.076*
C21	0.07270 (19)	0.7591 (3)	−0.39474 (9)	0.0756 (6)
H21A	0.0056	0.6915	−0.4162	0.091*
H21B	0.0303	0.8436	−0.3778	0.091*
C22	0.1496 (2)	0.8187 (2)	−0.44271 (9)	0.0883 (7)
H22A	0.2180	0.8831	−0.4215	0.132*
H22B	0.0935	0.8757	−0.4750	0.132*
H22C	0.1863	0.7350	−0.4622	0.132*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F	0.0586 (8)	0.1145 (11)	0.1030 (10)	0.0154 (7)	0.0347 (7)	−0.0070 (8)

N1	0.0966 (14)	0.0953 (15)	0.0443 (11)	0.0314 (10)	0.0222 (9)	0.0153 (10)
N2	0.0533 (12)	0.0938 (14)	0.0638 (12)	0.0117 (10)	0.0080 (9)	−0.0081 (10)
N3	0.0499 (10)	0.0481 (9)	0.0359 (9)	0.0020 (7)	0.0080 (7)	0.0045 (7)
C1	0.0471 (13)	0.0640 (14)	0.0584 (13)	0.0105 (10)	0.0230 (10)	0.0063 (11)
C2	0.0425 (12)	0.0657 (14)	0.0529 (13)	−0.0029 (10)	0.0036 (9)	0.0041 (11)
C3	0.0491 (12)	0.0540 (12)	0.0378 (10)	−0.0025 (9)	0.0058 (9)	−0.0035 (9)
C4	0.0431 (11)	0.0412 (11)	0.0308 (10)	0.0009 (8)	0.0064 (8)	0.0034 (8)
C5	0.0461 (12)	0.0481 (12)	0.0419 (11)	0.0000 (9)	0.0050 (9)	−0.0025 (9)
C6	0.0626 (14)	0.0568 (13)	0.0466 (12)	0.0067 (10)	0.0162 (10)	−0.0075 (10)
C7	0.0427 (11)	0.0378 (10)	0.0345 (10)	−0.0032 (8)	0.0069 (8)	−0.0035 (8)
C8	0.0423 (12)	0.0500 (12)	0.0327 (10)	0.0035 (8)	0.0078 (8)	−0.0015 (9)
C9	0.0554 (13)	0.0590 (13)	0.0364 (11)	0.0131 (9)	0.0051 (9)	−0.0009 (10)
C10	0.0531 (13)	0.0527 (12)	0.0360 (11)	0.0030 (10)	0.0001 (9)	−0.0029 (9)
C11	0.0445 (11)	0.0463 (11)	0.0389 (10)	0.0054 (8)	0.0104 (8)	0.0001 (9)
C12	0.0408 (10)	0.0416 (11)	0.0360 (10)	−0.0034 (8)	0.0077 (8)	−0.0014 (9)
C13	0.0591 (13)	0.0512 (12)	0.0338 (10)	0.0060 (10)	0.0136 (9)	0.0021 (9)
C14	0.0555 (12)	0.0523 (12)	0.0405 (11)	0.0069 (9)	0.0143 (9)	−0.0007 (9)
C15	0.0530 (12)	0.0501 (12)	0.0417 (11)	0.0074 (9)	0.0157 (9)	0.0048 (9)
C16	0.0606 (13)	0.0563 (13)	0.0370 (11)	0.0024 (10)	0.0169 (9)	0.0022 (10)
C17	0.0556 (12)	0.0484 (12)	0.0424 (11)	0.0014 (9)	0.0052 (9)	0.0074 (9)
C18	0.0687 (14)	0.0573 (13)	0.0498 (12)	−0.0091 (10)	0.0000 (10)	−0.0008 (10)
C19	0.0644 (15)	0.0843 (16)	0.0499 (12)	−0.0054 (11)	−0.0041 (10)	0.0061 (12)
C20	0.0703 (15)	0.0679 (15)	0.0481 (12)	−0.0004 (11)	0.0033 (10)	0.0008 (11)
C21	0.0822 (16)	0.0874 (17)	0.0520 (13)	−0.0048 (12)	−0.0011 (11)	0.0134 (12)
C22	0.1049 (19)	0.0948 (19)	0.0611 (15)	−0.0152 (14)	0.0048 (13)	0.0105 (13)

Geometric parameters (Å, °)

F—C1	1.3629 (19)	C13—C14	1.352 (2)
N1—C9	1.148 (2)	C13—H13A	0.9300
N2—C10	1.153 (2)	C14—H14A	0.9300
N3—C14	1.3493 (19)	C15—C16	1.349 (2)
N3—C16	1.353 (2)	C15—H15A	0.9300
N3—C17	1.4793 (19)	C16—H16A	0.9300
C1—C2	1.356 (2)	C17—C18	1.506 (2)
C1—C6	1.364 (2)	C17—H17A	0.9700
C2—C3	1.383 (2)	C17—H17B	0.9700
C2—H2A	0.9300	C18—C19	1.526 (2)
C3—C4	1.391 (2)	C18—H18A	0.9700
C3—H3A	0.9300	C18—H18B	0.9700
C4—C5	1.386 (2)	C19—C20	1.510 (2)
C4—C7	1.487 (2)	C19—H19A	0.9700
C5—C6	1.386 (2)	C19—H19B	0.9700
C5—H5A	0.9300	C20—C21	1.519 (2)
C6—H6A	0.9300	C20—H20A	0.9700
C7—C11	1.384 (2)	C20—H20B	0.9700
C7—C8	1.407 (2)	C21—C22	1.508 (2)
C8—C9	1.411 (2)	C21—H21A	0.9700
C8—C10	1.419 (2)	C21—H21B	0.9700

C11—C12	1.417 (2)	C22—H22A	0.9600
C11—H11A	0.9300	C22—H22B	0.9600
C12—C13	1.411 (2)	C22—H22C	0.9600
C12—C15	1.413 (2)		
C14—N3—C16	118.26 (14)	C16—C15—H15A	118.8
C14—N3—C17	121.48 (15)	C12—C15—H15A	118.8
C16—N3—C17	120.24 (14)	C15—C16—N3	121.49 (16)
C2—C1—F	118.64 (18)	C15—C16—H16A	119.3
C2—C1—C6	123.51 (17)	N3—C16—H16A	119.3
F—C1—C6	117.85 (18)	N3—C17—C18	111.79 (14)
C1—C2—C3	118.38 (17)	N3—C17—H17A	109.3
C1—C2—H2A	120.8	C18—C17—H17A	109.3
C3—C2—H2A	120.8	N3—C17—H17B	109.3
C2—C3—C4	120.85 (17)	C18—C17—H17B	109.3
C2—C3—H3A	119.6	H17A—C17—H17B	107.9
C4—C3—H3A	119.6	C17—C18—C19	112.70 (15)
C5—C4—C3	118.16 (15)	C17—C18—H18A	109.1
C5—C4—C7	121.33 (15)	C19—C18—H18A	109.1
C3—C4—C7	120.47 (15)	C17—C18—H18B	109.1
C6—C5—C4	121.53 (16)	C19—C18—H18B	109.1
C6—C5—H5A	119.2	H18A—C18—H18B	107.8
C4—C5—H5A	119.2	C20—C19—C18	115.26 (16)
C1—C6—C5	117.55 (17)	C20—C19—H19A	108.5
C1—C6—H6A	121.2	C18—C19—H19A	108.5
C5—C6—H6A	121.2	C20—C19—H19B	108.5
C11—C7—C8	120.62 (15)	C18—C19—H19B	108.5
C11—C7—C4	122.68 (14)	H19A—C19—H19B	107.5
C8—C7—C4	116.66 (14)	C19—C20—C21	112.76 (16)
C7—C8—C9	123.00 (16)	C19—C20—H20A	109.0
C7—C8—C10	120.83 (15)	C21—C20—H20A	109.0
C9—C8—C10	116.15 (15)	C19—C20—H20B	109.0
N1—C9—C8	178.3 (2)	C21—C20—H20B	109.0
N2—C10—C8	177.3 (2)	H20A—C20—H20B	107.8
C7—C11—C12	130.83 (16)	C22—C21—C20	112.99 (17)
C7—C11—H11A	114.6	C22—C21—H21A	109.0
C12—C11—H11A	114.6	C20—C21—H21A	109.0
C13—C12—C15	114.01 (15)	C22—C21—H21B	109.0
C13—C12—C11	127.40 (15)	C20—C21—H21B	109.0
C15—C12—C11	118.49 (16)	H21A—C21—H21B	107.8
C14—C13—C12	121.53 (16)	C21—C22—H22A	109.5
C14—C13—H13A	119.2	C21—C22—H22B	109.5
C12—C13—H13A	119.2	H22A—C22—H22B	109.5
N3—C14—C13	122.33 (17)	C21—C22—H22C	109.5
N3—C14—H14A	118.8	H22A—C22—H22C	109.5
C13—C14—H14A	118.8	H22B—C22—H22C	109.5
C16—C15—C12	122.35 (17)		
F—C1—C2—C3	179.02 (15)	C4—C7—C11—C12	14.2 (3)
C6—C1—C2—C3	−0.9 (3)	C7—C11—C12—C13	11.4 (3)

C1—C2—C3—C4	0.6 (3)	C7—C11—C12—C15	−172.34 (16)
C2—C3—C4—C5	0.6 (2)	C15—C12—C13—C14	1.1 (2)
C2—C3—C4—C7	178.29 (15)	C11—C12—C13—C14	177.44 (16)
C3—C4—C5—C6	−1.6 (2)	C16—N3—C14—C13	−0.1 (3)
C7—C4—C5—C6	−179.27 (15)	C17—N3—C14—C13	178.42 (15)
C2—C1—C6—C5	−0.1 (3)	C12—C13—C14—N3	−0.2 (3)
F—C1—C6—C5	−179.97 (15)	C13—C12—C15—C16	−1.7 (2)
C4—C5—C6—C1	1.4 (3)	C11—C12—C15—C16	−178.44 (16)
C5—C4—C7—C11	−125.40 (18)	C12—C15—C16—N3	1.6 (3)
C3—C4—C7—C11	57.0 (2)	C14—N3—C16—C15	−0.6 (3)
C5—C4—C7—C8	57.0 (2)	C17—N3—C16—C15	−179.09 (15)
C3—C4—C7—C8	−120.63 (17)	C14—N3—C17—C18	−99.45 (19)
C11—C7—C8—C9	−170.88 (16)	C16—N3—C17—C18	79.0 (2)
C4—C7—C8—C9	6.8 (2)	N3—C17—C18—C19	173.21 (15)
C11—C7—C8—C10	7.7 (2)	C17—C18—C19—C20	63.6 (2)
C4—C7—C8—C10	−174.63 (15)	C18—C19—C20—C21	173.53 (17)
C8—C7—C11—C12	−168.25 (17)	C19—C20—C21—C22	−175.80 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3A···N2^{i}	0.93	2.61	3.535 (3)	175
C16—H16A···N1^{ii}	0.93	2.51	3.354 (3)	151

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

Fig. 1

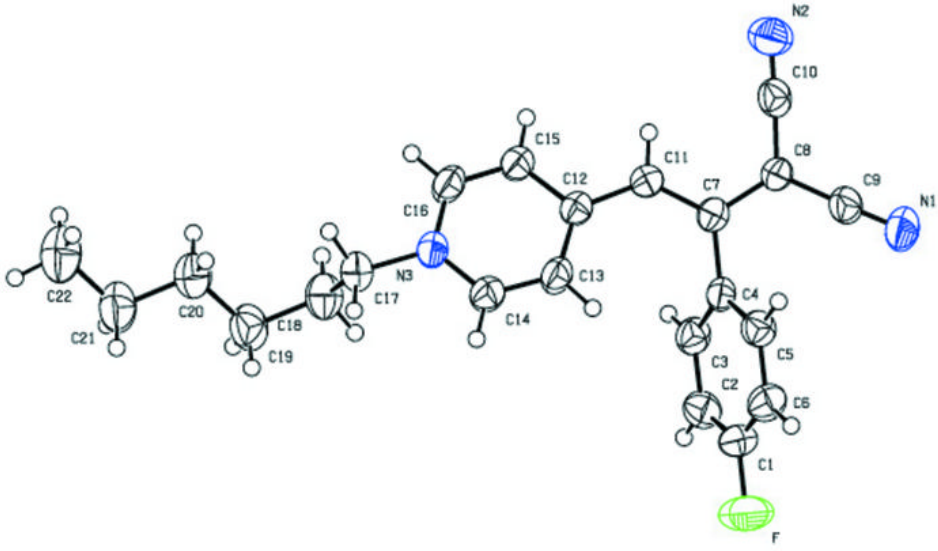

N2
C10
C15
C11
C8
C12
C7
C9
N1
C16
N3
C13
C4
C22
C17
C14
C20
C18
C21
C19
C3
C5
C2
C6
C1
F

Fig. 2

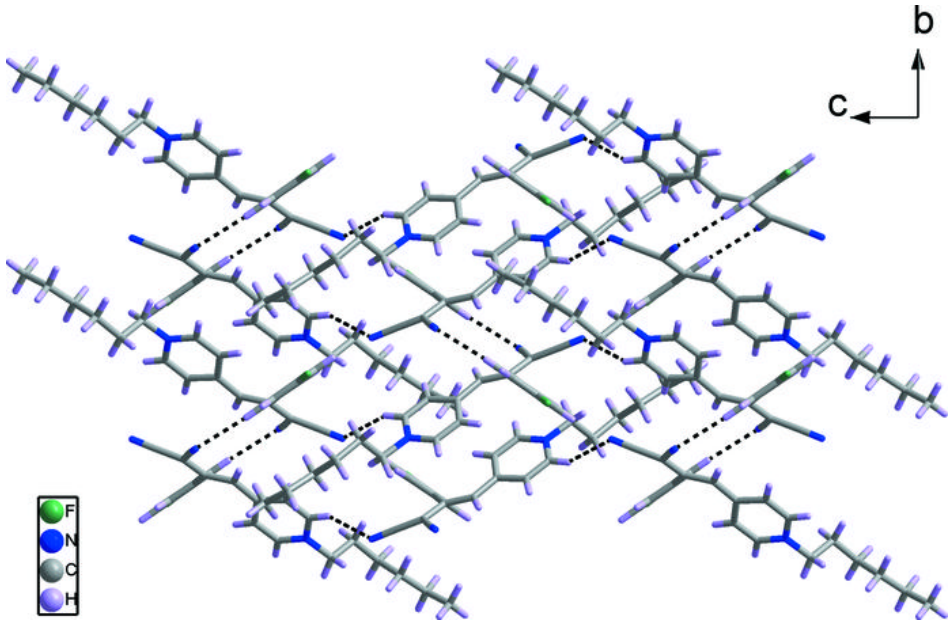


Fig. 3