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# (*E*)-2-[5-(3-Bromophenyl)pyrazol-3-yl]-3-(pyrrol-2-yl)acrylonitrile

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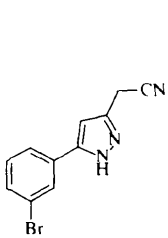
## Abstract

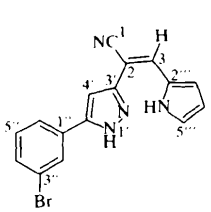
The title compound, $C_{16}H_{11}BrN_4$, has been isolated as its *E* isomer *via* the condensation of pyrrole-2-carboxaldehyde onto the active methylene of [5-(3-bromophenyl)pyrazol-3-yl]acetonitrile. It exhibits both intra- and intermolecular hydrogen bonding; the latter produces infinite one-dimensional chains of molecules.

## Comment

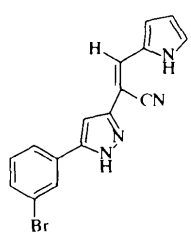
Pyrazole derivatives are well known to have applications in medicine, agriculture and industry (Ram *et al.*, 1993; Singh *et al.*, 1995). In the course of synthesizing a range of novel pyrazole derivatives (for structure–activity relationship studies) by incorporating a pyrrole moiety, pyrrole-2-carboxaldehyde was condensed onto the active methylene of pyrazole, (I); the motive for the incorporation of the pyrrole ring was that it is an integral component of haem and chlorophyll, and pyrrole-based compounds find widespread applications in medicinal chemistry. The stereochemistry around the newly created C=C double bond in the condensation product could not easily be established by any spectral technique, *i.e.* whether the product is (*E*)- or (*Z*)-2-[5-(3-bromophenyl)-pyrazol-3-yl]-3-(pyrrol-2-yl)acrylonitrile [(II) and (III), respectively]. The present study was undertaken in order to obtain unambiguous structural characterization of this novel condensation product.




(I)




(II)




(III)

The structure of the title compound, illustrated in Fig. 1, was solved in the space group *C*2 but then transformed into *Fdd*2; in this process the volume of the unit cell was doubled, but the number of molecules in the asymmetric unit was reduced from two to one. The observed structure is clearly that of the *E* isomer. The pyrrole and pyrazole rings are coplanar [angle between planes = 0.50 (4)°] and this may be largely attributed to strong intramolecular hydrogen bonding between N1‴ and N2′ [see Table 2, N1‴···N2′ 2.694 (6) Å; *cf.* sum of nitrogen van der Waals radii 3.10 Å]. In contrast, the phenyl ring is slightly twisted away from the pyrazole ring to give an interplanar angle of 13.19 (9)°. Weak intermolecular hydrogen bonding is proposed between the pyrazole ring N—H group and the N atom from the nitrile group of an adjacent molecule. This is assumed to be weaker than the intramolecular hydrogen bonding on the basis of atomic separations (Table 2). This interaction produces infinite one-dimensional chains of molecules along **c**. A search of the Cambridge Structural Database (Allen & Kennard, 1993) failed to reveal any other structures containing the 3-(pyrrol-2-yl)acrylonitrile unit.

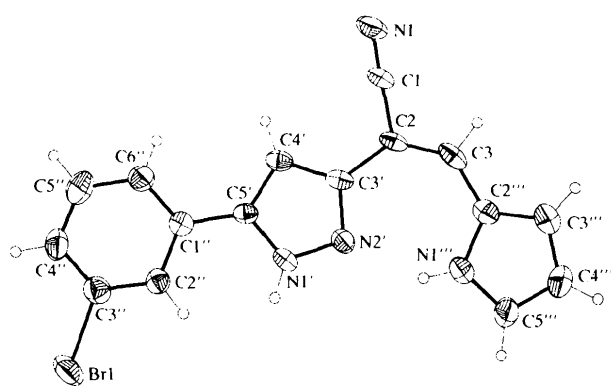



Fig. 1. View of the molecule showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are shown as circles of an arbitrary radius.

## Experimental

[5-(3-Bromophenyl)pyrazol-3-yl]acetonitrile [(I), 0.393 g, 1.5 mmol] was dissolved in ethanol (20 ml), sodium *tert*-butoxide (0.144 g, 1.5 mmol) was added and the solution stirred for 10 min. Pyrrole-2-carboxaldehyde (0.144 g, 1.5 mmol) was added and the progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the solution was concentrated under reduced pressure and the concentrate poured over crushed ice (20 g). The contents were stirred vigorously and a greenish-yellow solid precipitated out; it was filtered, washed with water, dried and column chromatographed on silica gel whereupon (*E*)-2-[5-(3-bromophenyl)pyrazol-3-yl]-3-(pyrrol-2-yl)acrylonitrile, (II), eluted out with ethyl acetate in petroleum ether (5% *v*/*v*). It crystallized from acetone as yellow needles (0.274 g, yield 54%), m.p. 483–484 K; UV (MeOH): 212, 257 and 356 nm; IR (Nujol): 3224, 2360, 2342, 2225, 1726, 1596, 1306, 1148, 1118, 1090, 1037, 1020, 967, 898, 884, 730 and 686 $cm^{-1}$; $^1H$ NMR (250 MHz, DMSO-$d_6$): $\delta$ 6.33 (1H, *bs*, C-4‴H), 6.79

(1H, *bs*, C-3‴H), 7.05 (1H, *s*, C-4′H), 7.29 (1H, *bs*, C-5‴H), 7.35 (1H, *s*, C-3H), 7.45 (1H, *t*, *J* = 7.9 Hz, C-5″H), 7.60 (1H, *d*, *J* = 8.2 Hz, C-4″H), 7.88 (1H, *d*, *J* = 7.9 Hz, C-6″H), 8.14 (1H, *bs*, C-2″H), 13.10 (1H, *bs*, C-1′H) and 13.90 p.p.m. (1H, *bs*, C-1‴H); $^{13}$C NMR (62.8 MHz, DMSO-$d_6$); $\delta$ 93.5, 103.1, 110.9, 119.4, 121.1, 122.4, 124.5, 127.7, 128.0, 130.3, 131.1, 131.4, 131.7, 142.0 and 145.9 p.p.m.; MS (EI; 70 eV) *m/z* (% rel. int.): 340 (18), 338 (19) [$M^+$], 289 (31), 287 (31), 250 (17), 229 (3), 218 (75), 185 (7), 156 (2), 154 (8), 125 (26), 109 (100), 77 (59), 65 (37) and 39 (29).

*Crystal data*

$C_{16}H_{11}BrN_4$
$M_r$ = 339.20
Orthorhombic
*Fdd*2
$a$ = 12.9598 (16) Å
$b$ = 53.600 (3) Å
$c$ = 8.2907 (12) Å
$V$ = 5759.1 (12) Å$^3$
$Z$ = 16
$D_x$ = 1.565 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 3755 reflections
$\theta$ = 2.95–25.00°
$\mu$ = 2.853 mm$^{-1}$
$T$ = 293 (2) K
Needle
0.50 × 0.10 × 0.10 mm
Pale yellow

*Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.440, $T_{max}$ = 0.752
7019 measured reflections
2266 independent reflections

1780 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.058
$\theta_{max}$ = 25°
$h = -14 \rightarrow 15$
$k = -48 \rightarrow 63$
$l = -9 \rightarrow 9$
Intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.099
$S$ = 0.994
2266 reflections
191 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.67 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (°)*

| | | | |
|---|---|---|---|
| N1—C1—C2 | 178.5 (7) | C3—C2—C3′ | 131.3 (5) |
| C3—C2—C1 | 115.1 (5) | C2—C3—C2‴ | 134.8 (5) |
| C5′—N1′—N2′—C3′ | 0.2 (6) | N1′—C5′—C1″—C6″ | 168.8 (5) |
| C1—C2—C3—C2‴ | 179.8 (6) | C2—C3—C2‴—N1‴ | −2.5 (11) |
| C3′—C2—C3—C2‴ | 1.3 (12) | | |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1‴—H1‴···N2′ | 0.86 | 1.949 | 2.694 (6) | 144.2 |
| N1′—H1′···N1ⁱ | 0.86 | 2.057 | 2.903 (7) | 167.5 |

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

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different $\varphi$ angle for the crystal and each exposure of 10 s covered 0.3° in $\omega$. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 99% complete to at least 25° in $\theta$. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections: no decay was observed.

The space group assigned to this structure, *Fdd*2, is non-centrosymmetric but with different enantiomers related *via* the *d* glide plane operations. The ambiguity in the absolute structure refers to the orientation with respect to the polar *c* axis: the value of the Flack (1983) parameter obtained [0.573 (17)] indicates twinning with both orientations present in approximately equal proportions.

H atoms were added at calculated positions and refined using a riding model. Anisotropic temperature factors were used for all non-H atoms. H atoms were given isotropic temperature factors equal to 1.2 (or 1.5 for methyl-H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at CLRC Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1286). Services for accessing these data are described at the back of the journal.

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