Absorption correction:
ψ scan (*XEMP*; Siemens, 1994)
T_{min} = 0.264, T_{max} = 0.371
5981 measured reflections
5650 independent reflections
3876 reflections with
$F > 4\sigma(F)$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 22$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.044
wR = 0.056
S = 0.986
3876 reflections
379 parameters
H atoms: see below
$w = 1/(0.52883 + 0.00952F_o + 0.00037F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 0.254 e Å^{-3}
$\Delta\rho_{min}$ = −0.271 e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected torsion angles (°)*

C3—C4—C7—C8	141.8 (3)
C3—C4—C7—C17	−103.7 (3)
C5—C4—C7—C8	−42.3 (4)
C5—C4—C7—C17	72.1 (3)
C105—C104—C107—C108	135.5 (3)
C105—C104—C107—C117	−108.1 (3)
C103—C104—C107—C108	−45.9 (4)
C103—C104—C107—C117	70.5 (3)

Each H atom was assigned the equivalent isotropic displacement parameter of the parent C atom and allowed to ride (0.96 Å). The H atom of C107 was localized in a difference Fourier map and refined keeping U_{iso} fixed.

Data collection: Syntex diffractometer software. Cell refinement: Syntex diffractometer software. Data reduction: Syntex diffractometer software. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994). Program(s) used to refine structure: *CAOS* (Camalli & Spagna, 1994). Molecular graphics: *VIEW* (Carrell, 1994). Software used to prepare material for publication: *CAOS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1053). Services for accessing these data are described at the back of the journal. A figure showing the superposition of the two molecules in the asymmetric unit has also been deposited.

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Acta Cryst. (1998). C**54**, 844–846

[1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-pyrazol-5-yl]acetonitrile

SANJAY MALHOTRA,[a] ARCHANA VATS,[a] VIRINDER S. PARMAR[a] AND WILLIAM ERRINGTON[b]

[a]*Department of Chemistry, University of Delhi, Delhi 110 007, India, and* [b]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: w.errington@warwick.ac.uk*

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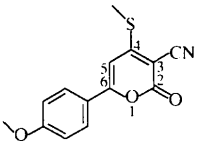
Abstract

The title compound, $C_{18}H_{14}ClN_3O$, was obtained as one of the products from the condensation of 4-chlorophenylhydrazine hydrochloride with 6-(4-methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile. The best planes through the phenyl rings in the methoxyphenyl and chlorophenyl groups are aligned at angles of 7.02 (8) and 56.19 (4)°, respectively, relative to the pyrazole ring.

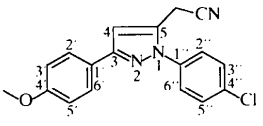
Comment

Pyrazole derivatives are principally used in medicine; many alkyl pyrazoles have shown quite significant bacteriostatic, bacteriocidal and fungicidal actions (Herrman & Grabliks, 1961; Rich & Horsfall, 1952; McNew & Sundholm, 1949). Nitrogen heterocycles,

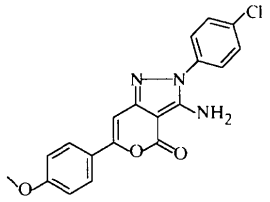
such as pyrazoles, imidazoles and triazoles, either in isolation or in fused systems, are well documented for their antifertility activity (Omodei-Sale *et al.*, 1976). Consequently, we have synthesized several diphenylpyrazolylacetonitriles for structure–activity relationship studies. In this investigation, 4-chlorophenylhydrazine hydrochloride was condensed with 6-(4-methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile, (I), in pyridine at 389 K to afford two different compounds, *i.e.* (II) and (III), in one step. The point of attachment of the 4-chlorophenyl group to the pyrazole nucleus in (II)



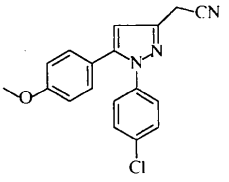
(I)



(II)



(III)



(IV)

could not be confirmed by spectroscopic data, *i.e.* the possibility of structure (IV) for this compound could not be ruled out; the aim of this X-ray investigation was to resolve this problem.

The molecular structure of the title compound is illustrated in Fig. 1. Bond lengths and angles are unexceptional; specifically, the acetonitrile group is normal, with a C—C—N bond angle of 179.3 (2)°. The phenyl rings in the methoxyphenyl and chlorophenyl groups are aligned at angles of 7.02 (8) and 56.19 (4)°, respectively, with respect to the least-squares plane through the pyrazole ring. The methoxy group is almost coplanar with its attached phenyl group, as shown by the C7′—O1—C4′—C3′ torsion angle of 170.19 (17)°; similarly the acetonitrile group is coplanar with the plane of the pyrazole ring [the N1—C5—C6—C7 torsion angle is 179.27 (16)°]. Related pyrazole acetonitrile derivatives have been reported previously by this group (Singh *et al.*, 1995; Malhotra *et al.*, 1997).

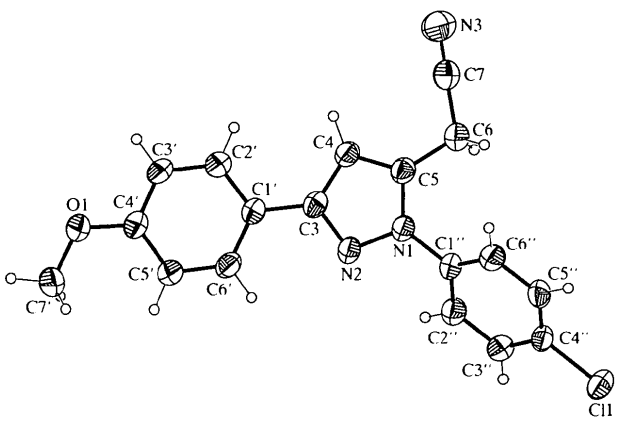


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms have small arbitrary radii for clarity.

Experimental

4-Chlorophenylhydrazine hydrochloride (1.432 g, 0.008 mol) was added to a preheated suspension of (I) (1.092 g, 0.004 mol) at 335 K in dry pyridine (50 ml) and the reaction mixture was refluxed for 6 h at 389 K. After removal of pyridine under reduced pressure, the crude product was taken up in ethyl acetate, washed with water and dilute HCl, and dried over anhydrous Na_2SO_4. On removal of ethyl acetate, the crude reaction mixture was column chromatographed (chloroform/petroleum ether 1:4) to afford compound (II), which recrystallized from acetone as needle-shaped crystals (396 mg, 27% yield), m.p. 416–417 K. IR (nujol) ν_{max}: 2220 (C≡N), 1620, 1535, 1495, 1370, 1250, 1170, 1090, 1020, 840, 790, 730 and 620 cm^{-1}. UV (MeOH) λ_{max}: 291, 265 and 236 nm. ^1H NMR (250 MHz, DMSO-d_6): δ 3.75 (*s*, 3H, $-OCH_3$), 4.32 (*s*, 2H, $-CH_2CN$), 6.81 (*s*, 1H, H4), 6.99 (*d*, 2H, J = 7.8 Hz, H2′ and H6′), 7.17 (*s*, 4H, H2″, H3″, H5″ and H6″), 7.75 (*d*, 2H, J = 7.8 Hz, H3′ and H5′). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ 15.51 (CH_2CN), 55.07 (OCH_3), 104.85 (C4), 114.10 (C3′ and C5′), 116.84 (CH_2CN), 124.68 (C1′), 126.14 (C3″ and C5″), 126.69 (C2′ and C6′), 129.35 (C2″ and C6″), 132.54 (C1″), 137.51 (C3), 150.98 (C5) and 159.33 (C4′). EIMS *m/z* (% int.): 324/326 ([M + 1]$^+$, 21/6), 323/325 ([M^+], 100/33), 308/310 (14/5), 279 (4), 244 (3), 205 (2), 111/113 (9/3) and 75 (8).

Crystal data

$C_{18}H_{14}ClN_3O$
M_r = 323.77
Orthorhombic
$P2_12_12_1$
a = 7.753 (2) Å
b = 11.126 (2) Å
c = 18.281 (3) Å
V = 1576.9 (5) Å^3
Z = 4
D_x = 1.364 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6894 reflections
θ = 2.14–28.57°
μ = 0.250 mm^{-1}
T = 220 (2) K
Block
0.48 × 0.42 × 0.35 mm
Colourless

Data collection

Siemens SMART CDD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.887, T_{max} = 0.916
9362 measured reflections

3676 independent reflections (includes Friedel pairs)
3203 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.57°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 6$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.080$
$S = 1.037$
3676 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0390P)^2 + 0.1372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.147$ e Å^{-3}
$\Delta\rho_{min} = -0.160$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.018 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.03 (5)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C4''	1.7423 (15)	N1—C1''	1.4311 (18)
O1—C4'	1.3761 (18)	N2—C3	1.3377 (18)
O1—C7'	1.423 (2)	N3—C7	1.132 (3)
N1—C5	1.363 (2)	C3—C4	1.407 (2)
N1—N2	1.3650 (17)	C4—C5	1.366 (2)
C5—N1—N2	111.97 (12)	N1—C5—C4	106.50 (14)
C3—N2—N1	104.66 (12)	N1—C5—C6	121.71 (13)
N2—C3—C4	110.97 (13)	N3—C7—C6	179.3 (2)
C5—C4—C3	105.90 (14)		
N1—C5—C6—C7	179.27 (16)	C7'—O1—C4'—C3'	170.19 (17)
N2—C3—C1'—C6'	−6.6 (2)	N2—N1—C1''—C2''	57.7 (2)

The temperature of the crystal was controlled using an 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 φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 93% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections; it was found to be negligible. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their parent atoms.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). 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, England (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: CF1231). Services for accessing these data are described at the back of the journal.

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3,4,5,6-Tetrafluoro-1,2,7,8-tetrakis(trifluoromethyl)phenanthrene and 3,4,7,8-Tetrafluoro-1,2,5,6-tetrakis(trifluoromethyl)anthracene

Dale C. Swenson, Michiharu Yamamoto and Donald J. Burton

Department of Chemistry, University of Iowa, Iowa City, Ia 52242, USA. E-mail: dale-swenson@uiowa.edu

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Abstract

A photocyclization reaction produces two isomers of $C_{18}H_2F_{16}$. Crystal structures show the major product to be 3,4,5,6-tetrafluoro-1,2,7,8-tetrakis(trifluoromethyl)phenanthrene, (1), and the minor product to be 3,4,7,8-tetrafluoro-1,2,5,6-tetrakis(trifluoromethyl)-anthracene, (2). The phenanthrene skeleton in (1) is distorted from planarity by steric interaction between the 4- and 7-F atoms. Compound (2) is centered on an inversion center; the anthracene skeleton is nearly planar,