

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-[3-(4-Bromophenyl)-1-phenylpyrazol-5-yl]-2H-1-benzopyran-2-one

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Abstract

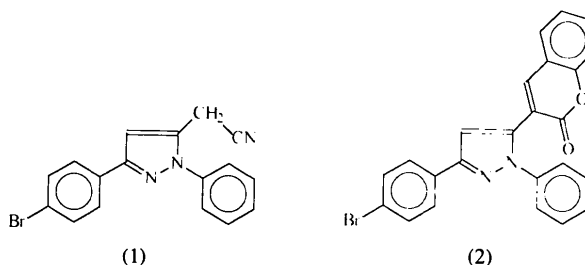
In the title compound, C₂₄H₁₅BrN₂O₂, the angles formed by the planes of the bromophenyl, phenyl and coumarin groups with the plane of the pyrazole nucleus are 19.3, 38.8 and 65.6°, respectively. The absolute structure has been determined.

Comment

Many compounds containing the pyrazole nucleus are used as drugs, insecticides and pesticides (Weily & Wiley, 1964; Taki, Meki, Fujimoto, Umeda & Imahase, 1992). Consequently, we have synthesized several diphenyl-substituted pyrazolylacetonitriles [*e.g.* compound (1)] and have established that such compounds have strong anti-invasive activity against solid tumours. The presence of a reactive methylene group in these pyrazole derivatives can be used in various ways to syn-

thesize compounds containing the pyrazole moiety and with the potential for biological activity.

In this investigation, salicylaldehyde was condensed with the pyrazole (1) to produce the coumarin derivative (2). The point of attachment of the coumarin group to the pyrazole nucleus was confirmed using ¹H NMR and mass spectrometry. The aim of this X-ray investigation was to obtain further structural information regarding the orientations of the groups attached to the pyrazole nucleus.



The molecular structure, as determined in this investigation, is illustrated in Fig. 1. The pyrazole nucleus is flat within experimental error, and the planar peripheral phenyl and bromophenyl groups are inclined with respect to the pyrazole plane at angles of 38.8 (6) and 19.3 (7)°, respectively. The coumarin unit is not exactly flat, but the least-squares plane through the ring atoms, with r.m.s. deviation 0.023 Å, is inclined at an angle of 65.6 (4)° to the plane of the pyrazole nucleus.

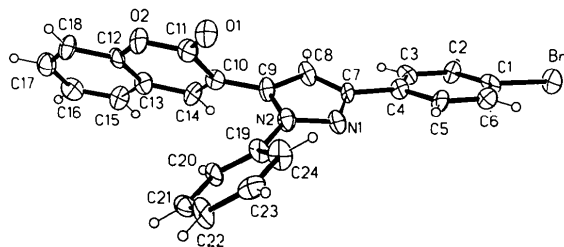


Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level.

The propeller-like orientations of the peripheral groups give a chiral molecule. The observed value of the absolute structure parameter (Flack, 1983) is $-0.02(3)$. This is within one e.s.d. of zero and its e.s.d. is also relatively small; thus it provides strong evidence that the absolute structure has been assigned correctly. All bond lengths and angles are unexceptional. The generally low precision associated with the determination is due to poor crystal quality.

Experimental

Salicylaldehyde (0.13 ml, 0.0012 mol) was added to a solution of (1) (0.34 g, 0.001 mol) in ethanol (20 ml). After the

addition of a drop of aqueous sodium hydroxide (10%), the reaction mixture was refluxed for 4 h, cooled and neutralized with hydrochloric acid. The white solid that precipitated was recrystallized from petrol (60–80°)–benzene (3:1) to give white crystals of (2) (0.4 g, 90%), m.p. 510 K.

Crystal data

$C_{24}H_{15}BrN_2O_2$

$M_r = 443.29$

Monoclinic

Cc

$a = 22.031 (18) \text{ \AA}$

$b = 14.474 (18) \text{ \AA}$

$c = 6.002 (5) \text{ \AA}$

$\beta = 90.42 (10)^\circ$

$V = 1914 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.538 \text{ Mg m}^{-3}$

Data collection

Siemens P3R3 diffractometer

ω – 2θ scans

Absorption correction:

none

2458 measured reflections

1308 independent reflections

1037 observed reflections

$[I > 2\sigma(I)]$

$R_{int} = 0.0732$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0612$

$wR(F^2) = 0.1623$

$S = 1.062$

1304 reflections

262 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 15

reflections

$\theta = 5\text{--}8^\circ$

$\mu = 2.171 \text{ mm}^{-1}$

$T = 220 (2) \text{ K}$

Block

$0.13 \times 0.08 \times 0.08 \text{ mm}$

White

$\theta_{max} = 22.55^\circ$

$h = -23 \rightarrow 23$

$k = -15 \rightarrow 15$

$l = -6 \rightarrow 0$

3 standard reflections

monitored every 200

reflections

intensity decay: none

$\Delta\rho_{max} = 0.862 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -1.210 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

$= -0.02 (3)$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	x	y	z	U_{eq}
Br1	0.7396 (3)	0.40345 (10)	0.7532 (9)	0.0374 (5)
O1	0.3624 (5)	0.4220 (7)	1.7844 (19)	0.036 (3)
O2	0.2671 (5)	0.4170 (7)	1.6750 (17)	0.032 (3)
N1	0.5013 (6)	0.2846 (8)	1.434 (2)	0.028 (3)
N2	0.4427 (6)	0.2840 (9)	1.500 (2)	0.031 (3)
C1	0.6665 (5)	0.3886 (4)	0.9180 (17)	0.028 (3)
C2	0.6125 (5)	0.4170 (6)	0.8243 (16)	0.025 (3)
C3	0.5595 (6)	0.4041 (7)	0.943 (2)	0.026 (3)
C4	0.5612 (6)	0.3633 (7)	1.1522 (17)	0.024 (3)
C5	0.6165 (6)	0.3353 (7)	1.242 (2)	0.028 (3)
C6	0.6696 (5)	0.3479 (6)	1.125 (2)	0.029 (3)
C7	0.5025 (7)	0.3482 (10)	1.274 (2)	0.020 (3)
C8	0.4478 (7)	0.3867 (10)	1.237 (2)	0.030 (4)
C9	0.4074 (7)	0.3471 (11)	1.381 (2)	0.027 (4)
C10	0.3435 (7)	0.3625 (10)	1.421 (2)	0.026 (3)
C11	0.3262 (7)	0.4023 (11)	1.635 (3)	0.032 (4)

C12	0.2226 (6)	0.3970 (4)	1.514 (2)	0.028 (3)
C13	0.2381 (7)	0.3613 (6)	1.3085 (17)	0.030 (3)
C14	0.3006 (8)	0.3445 (12)	1.264 (3)	0.031 (4)
C15	0.1905 (5)	0.3406 (8)	1.165 (2)	0.032 (4)
C16	0.1303 (6)	0.3541 (7)	1.220 (2)	0.038 (3)
C17	0.1177 (7)	0.3899 (7)	1.4277 (19)	0.037 (3)
C18	0.1633 (5)	0.4120 (6)	1.578 (2)	0.034 (3)
C19	0.4242 (3)	0.2193 (6)	1.6712 (15)	0.030 (3)
C20	0.3688 (4)	0.1765 (7)	1.6512 (13)	0.032 (3)
C21	0.3507 (5)	0.1146 (8)	1.8218 (19)	0.038 (3)
C22	0.3894 (4)	0.0998 (9)	2.001 (2)	0.041 (4)
C23	0.4451 (7)	0.1435 (8)	2.0190 (19)	0.035 (3)
C24	0.4631 (6)	0.2054 (7)	1.8481 (18)	0.037 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br1—C1	1.907 (12)	C7—C8	1.35 (2)
O1—C11	1.23 (2)	C8—C9	1.37 (2)
O2—C11	1.34 (2)	C9—C10	1.45 (2)
O2—C12	1.40 (2)	C10—C14	1.36 (2)
N1—C7	1.33 (2)	C10—C11	1.46 (2)
N1—N2	1.35 (2)	C12—C18	1.382 (7)
N2—C9	1.39 (2)	C12—C13	1.384 (7)
N2—C19	1.45 (2)	C13—C15	1.384 (7)
C4—C7	1.51 (2)	C13—C14	1.43 (2)
C11—O2—C12	121.2 (10)	C7—C8—C9	107.8 (14)
C7—N1—N2	103.8 (11)	C8—C9—N2	103.5 (12)
N1—N2—C9	112.3 (11)	N2—C9—C10	123.8 (12)
N1—N2—C19	118.8 (11)	C14—C10—C9	122.0 (14)
C9—N2—C19	128.8 (10)	C14—C10—C11	120.1 (14)
C2—C1—Br1	119.0 (7)	C9—C10—C11	117.8 (13)
C6—C1—Br1	118.7 (8)	O1—C11—O2	117.1 (13)
C5—C4—C7	121.5 (10)	O1—C11—C10	124.2 (13)
C3—C4—C7	118.9 (10)	O2—C11—C10	118.7 (13)
N1—C7—C8	112.6 (12)	C18—C12—O2	115.8 (8)
N1—C7—C4	118.2 (11)	C13—C12—O2	121.1 (9)
C8—C7—C4	129.1 (12)	C20—C19—N2	118.9 (9)

The aromatic rings were restrained to be flat. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the C atom to which it is attached. Floating-origin constraints were imposed automatically.

Data collection: Siemens P3R3 system. Cell refinement: Siemens P3R3 system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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