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1-Acetyl-5-(2-methoxyphenyl)-3-(2-methoxystyryl)-2-pyrazoline

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.139
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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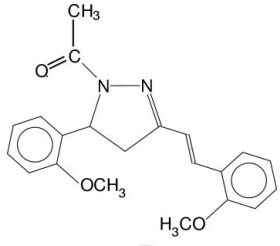
In the title compound, $C_{21}H_{22}N_2O_3$, the geometry of the heterodiene (N=C—C=C) indicates the presence of a resonance effect across the C—C bond. The heterodiene prefers the *s-trans* configuration. The molecules aggregate as double layers parallel to the (101) plane. Consecutive layers, labelled *ABAB* . . . , are inversely related to one another.

Comment

Pyrazolines and their derivatives display various biological properties, such as pesticidal, fungicidal, insecticidal, anti-inflammatory, anti-arthritic, antidepressant and antiviral activities, and have industrial applications, such as use as optical brighteners and polymer intermediates (Wang *et al.*, 1995; El-Hashash *et al.*, 1995). X-ray analysis of the title compound, (I) (Fig. 1), was undertaken as part of a series of investigations being carried out to study the influence of the variation in the substituent group on the conformation and packing modes of pyrazolines. In this context, the crystal structure of 1-acetyl-5-phenyl-3-styryl-2-pyrazoline (PYRA1; Krishnakumar *et al.*, 1998), 1-acetyl-5-(4-methoxyphenyl)- 3-(4-methoxystyryl)-2-pyrazoline (PYRA2) and 1-acetyl-5-(2-chlorophenyl)-3-(2-chlorostyryl)-2-pyrazoline (PYRA3; Krishnakumar *et al.*, 1999) have already been carried out.



(I)

The relatively short C1—C6 bond distance [1.438 (2) Å, *cf.* 1.444 (4) and 1.443 (4) Å in PYRA1, 1.442 (2) Å in PYRA2, and 1.456 (5) Å in PYRA3] is ascribable to the resonance between the C1=N2 and C6=C7 bonds. This resonance is supported by the fact that the five-membered dinitrogen heterocyclic ring, ethenyl atoms C6 and C7, and the aryl ring of the styryl group are approximately coplanar. The twist of the aryl ring of the styryl group with respect to the heterocyclic ring is 12.07 (13)° and is significantly different from that observed in the chloro-substituted analogue PYRA3 (23°). This difference may be attributed to the nature of the substituents and their consequent effect in inhibiting or promoting the resonance effect across the diene. A comparison of the influence of the 2- and 4-substituents in the aryl ring of the styryl group reveals that, in the case of the former,

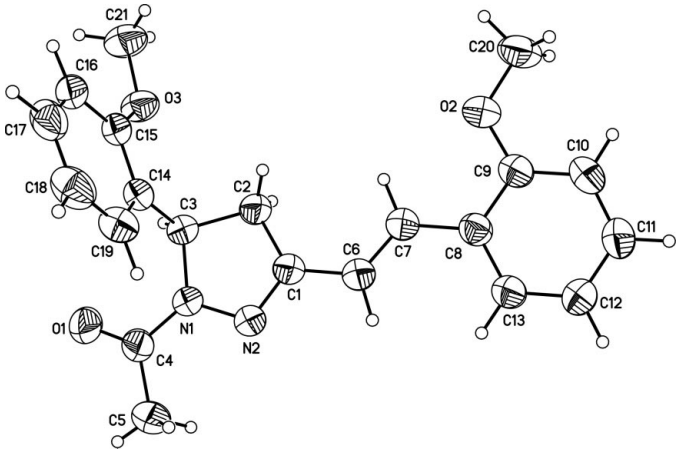


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

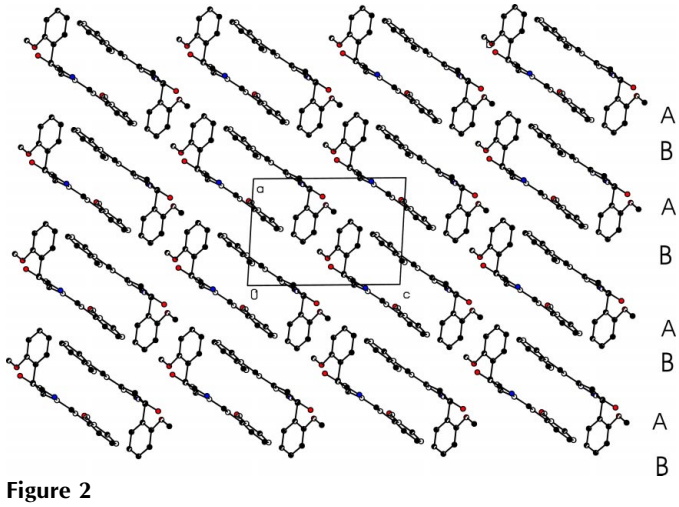


Figure 2
The molecular packing of (I), viewed down the *b* axis.

the resonance effect of the substituent is less transmitted to the imine N atom than that observed for the 4-analogue. The ^{15}N NMR spectrum [in $CDCl_3$ at natural abundance at 36.50 MHz, using a non-refocused INEPT sequence optimized for $J(^{15}N,H) = 10$ and 4 Hz], measured with a view to obtaining information on structural and bonding aspects of the pyrazolines, shows that the chemical shift of the sp^2 imine atom N1 depends significantly on the position and nature of the substituent in the styryl aromatic ring, while the sp^3 amide atom N2 remains insensitive to variation in substituents as it cannot enter into any resonance interaction with the aryl rings. The torsion angle about the heterodiene [N2═C1—C6═C7 = −178.3 (2)°] indicates that it prefers the *s-trans* configuration.

All the rings in (I) are essentially planar and their geometry is independent of the nature of the substituents. The packing in (I) has no correlation with the packing in PYRA1, PYRA2 and PYRA3. The molecules aggregate as double layers parallel to the (101) plane, as shown in Fig. 2. It is interesting to note that consecutive layers, labelled *ABAB*..., are inversely related to one another.

Experimental

Crystals of (I) were obtained from its saturated solution in methanol by slow evaporation at room temperature. Details of the synthesis have been described by Vijayabaskar (1997). Analysis found: C 71.89, H 6.39, N 8.03% (M^+ 350); calculated for $C_{21}H_{22}N_2O_3$: C 71.98, H 6.33, N 7.99% (M^+ 350).

Crystal data

$C_{21}H_{22}N_2O_3$
$M_r = 350.41$
Triclinic, $P\overline{1}$
$a = 8.8485$ (11) Å
$b = 8.9259$ (7) Å
$c = 12.9652$ (15) Å
$\alpha = 70.074$ (9)°
$\beta = 81.597$ (10)°
$\gamma = 75.041$ (8)°
$V = 928.17$ (17) Å^3
$Z = 2$
$D_x = 1.254$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 21$–46°
$\mu = 0.68$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.24 × 0.18 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.86$, $T_{max} = 0.92$
3750 measured reflections
3507 independent reflections
3058 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 69.9°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 1 h
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.139$
$S = 1.08$
3507 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.3268P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0170 (13)

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.218 (2)	C6—C7	1.332 (2)
O2—C13	1.361 (2)	C7—C8	1.462 (2)
O2—C20	1.416 (2)	C8—C9	1.396 (2)
O3—C19	1.371 (2)	C8—C13	1.404 (2)
O3—C21	1.419 (2)	C9—C10	1.377 (3)
N1—C4	1.361 (2)	C10—C11	1.372 (3)
N1—N2	1.385 (2)	C11—C12	1.376 (3)
N1—C3	1.474 (2)	C12—C13	1.386 (3)
N2—C1	1.292 (2)	C14—C15	1.381 (2)
C1—C6	1.438 (2)	C14—C19	1.394 (2)
C1—C2	1.505 (2)	C15—C16	1.391 (3)
C2—C3	1.539 (2)	C16—C17	1.368 (3)
C3—C14	1.512 (2)	C17—C18	1.378 (3)
C3—H3	0.9800	C18—C19	1.384 (2)
C4—C5	1.502 (3)	C18—H18	0.9300
N2—C1—C6—C7	−178.25 (18)	C1—C6—C7—C8	−176.72 (17)
C2—C1—C6—C7	4.8 (3)		

H atoms were treated as riding, with C—H distances of 0.93–0.97 Å and U_{iso}(H) values equal to 1.2–1.5 times U_{eq}(C).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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