ignored. Corrections were made for anomalous dispersion (Cromer & Liberman, 1970). A difference map calculated at the conclusion of the refinement had no chemically significant features.

The author thanks Dr Feldman for providing the crystals of the title compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BR1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-(*p*-Anisidino)-4-cyano-2,3-dihydro-3-pyrazolone Hemihydrate, $C_{11}H_{10}N_4O_2.0.5H_2O$

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Abstract

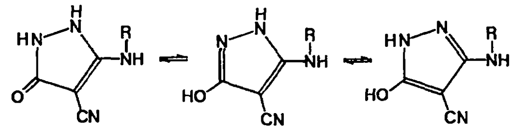
The title compound exists entirely in the keto form in the solid state, although NMR spectroscopy indicates that in solution the enol form is present. The asymmetric unit contains two structurally similar independent molecules and a water molecule of solvation. There is an extensive three-dimensional network of intermolecular hydrogen bonds of types N—H···O, N—H···N and *OW*—H···O.

Comment

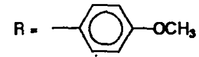
Pyrazole derivatives have been found to have moderate antimalarial activity (Garg, Singhal & Mathur, 1973). A number of derivatives of pyrazoles and several other heterocycles were synthesized and tested during a research project aimed at finding new antimalarial drugs which are more active or less toxic than those currently in use (Charris, 1993). The title compound, (I), was prepared as a part of that project, but was found to have no antimalarial activity.

The structure analysis showed that the asymmetric unit contains two independent molecules of (I) and a water molecule of solvation. The two organic molecules (labelled *a* and *b*) are structurally similar and only three bond distances differ by more than three e.s.d.'s: O2—C7 (3.3σ), N1—N2 (3.8σ) and N2—C1 (5.8σ).

In solution, the keto form (I) can exist in tautomeric equilibrium with enol forms (II) and (III). Indeed, the NMR spectrum in solution (see *Experimental*) shows an absorption corresponding to an OH group. However, in the crystal structure, the molecules are in the keto form, as shown by the bond length pattern of the five-membered ring, the C═O distance, the positions of the H atoms and the hydrogen-bonding scheme. In addition, the solid-state IR spectrum (see *Experimental*) shows an absorption assigned to a C═O stretch.



(I) (II) (III)



The bond lengths in the five-membered rings (mean values N1—N2 1.405, N1—C3 1.346, N2—C1 1.369, C1—C2 1.426, C2—C3 1.397 Å) are similar to those observed in several other pyrazolones (Mogensen & Simonsen, 1991, and references therein) and are significantly different from the values observed in pyrazole rings (Allen *et al.*, 1987). Moreover, the endo- and exocyclic bond angles do not follow the rules described by Bonati & Bovio (1990) for pyrazole rings. The C═O distances (mean value 1.255 Å) are also comparable to those found in pyrazolones (Mogensen & Simonsen, 1991, and references therein) and are significantly shorter than the value of 1.333 Å expected for enols (Allen *et al.*, 1987).

The N3—C3 distances (mean 1.343 Å) are significantly shorter than the N3—C4 bond lengths (mean 1.437 Å). Since N3 is planar, the former values can be compared with the value of 1.339 Å tabulated for planar C═C—NH—C moieties (Allen *et al.*, 1987), but the N3—C4 distances are too long when compared with the value of 1.353 Å for planar C_{aryl}—NH—C moieties (Allen *et al.*, 1987).

The five-membered rings deviate more from planarity (mean deviations from the plane are 0.022 and 0.031 Å for *a* and *b*, respectively) than the phenyl rings (0.003 and 0.006 Å, respectively). The methoxy groups lie close to the planes of the phenyl rings (dihedral angles 6.2 and 1.7° for *a* and *b*, respectively). The main difference in the geometry of the two independent molecules lies in the mutual orientation of the ring systems (inter-ring dihedral angles 86.8 and 57.6° for *a* and *b*, respectively), which is probably the result of packing forces.

All H atoms were located in difference Fourier maps and refined satisfactorily. In the crystal structure, there is an extensive three-dimensional network of intermolecular hydrogen bonds. The organic molecules are linked to their neighbours either directly, by bonds of types N—H···O and N—H···N, or *via* the solvent molecules by means of N—H···*OW*—H···O interactions. Among the direct bonds, a pair of N2—H2···O1 bonds connect two independent molecules, forming a dimer which contains a hydrogen-bonded ring. It has been suggested (Gilli, 1992, and references therein) that the formation of such rings leads to so-called resonance-assisted hydrogen bonding.

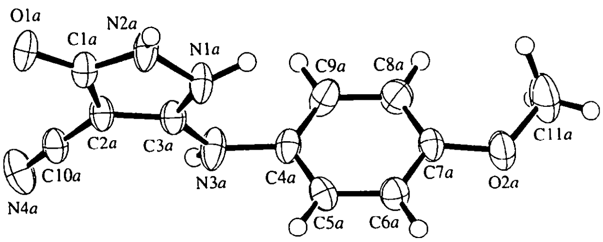


Fig. 1. Molecular structure of (I) (molecule *a*) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

To a solution of methyl 3-(*p*-anisidino)-2-cyano-3-methylthioacrylate, $MeOC_6H_4NHC(SMe){=}C(CN)CO_2Me$, [1019 mg, 3.7 mmol, prepared by the method of Tominaga, Michioka, Moriyama & Hosomi (1990)] in methanol (5.0 ml) was added hydrazine hydrate, $N_2H_4.H_2O$ (185 mg, 3.7 mmol). The solution was heated under reflux for 1 h. Removal of solvent *in vacuo* produced (I) (335 mg, 1.4 mmol, 38% yield) as a white solid, m.p. 514 K. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

Spectroscopic data: IR (KBr pellet) 2208 (CN), 1600 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$/DMSO-d_6/TMS) 3.78 (1H, *s*, OCH_3), 4.31 (1H, *bs*, OH), 6.84 (2H, *d*, *J* = 8.40 Hz, C5—H, C9—H), 7.22 (2H, *d*, *J* = 8.40 Hz, C6—H, C8—H), 7.71 (1H, *s*, NH), 8.68 p.p.m. (1H, *s*, NH).

Crystal data

$C_{11}H_{10}N_4O_2.0.5H_2O$
$M_r = 239.23$
Triclinic
$P\bar{1}$
$a = 10.55$ (2) Å
$b = 12.26$ (2) Å
$c = 9.76$ (2) Å
$\alpha = 113.1$ (1)°
$\beta = 99.1$ (2)°
$\gamma = 99.0$ (2)°
$V = 1113$ (4) Å^3
$Z = 4$
$D_x = 1.427$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 22 reflections
$\theta = 10.2$–18.1°
$\mu = 0.105$ mm^{-1}
$T = 295$ (1) K
Prism
0.26 × 0.20 × 0.16 mm
Colorless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5397 measured reflections
5118 independent reflections
2025 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.051$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity decay: 3.74%

Refinement

Refinement on *F*
$R = 0.0388$
$wR = 0.0389$
$S = 1.574$
2025 reflections
404 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
O1*a*	0.4505 (2)	0.4295 (2)	0.7453 (2)	0.0394 (1)
O1*b*	0.7445 (2)	0.3331 (2)	0.1943 (3)	0.0412 (1)
O2*a*	−0.0629 (2)	0.3629 (2)	−0.2056 (3)	0.0467 (1)
O2*b*	0.0243 (3)	0.1189 (2)	−0.6897 (3)	0.0577 (1)
N1*a*	0.2599 (3)	0.4258 (3)	0.4185 (3)	0.0382 (1)
N1*b*	0.4829 (3)	0.2847 (2)	−0.1025 (3)	0.0325 (1)
N2*a*	0.2973 (3)	0.4610 (3)	0.5765 (3)	0.0403 (1)
N2*b*	0.5899 (3)	0.3614 (3)	0.0236 (3)	0.0347 (1)
N3*a*	0.3023 (3)	0.2809 (3)	0.1988 (3)	0.0433 (1)
N3*b*	0.4153 (3)	0.0754 (3)	−0.2715 (3)	0.0357 (1)
N4*a*	0.5718 (3)	0.1909 (3)	0.4094 (4)	0.0530 (1)
N4*b*	0.6651 (3)	−0.0239 (3)	−0.0371 (3)	0.0481 (1)
C1*a*	0.3943 (3)	0.4083 (3)	0.6104 (4)	0.0329 (1)
C1*b*	0.6545 (3)	0.2895 (3)	0.0741 (4)	0.0296 (1)
C2*a*	0.4140 (3)	0.3316 (3)	0.4661 (4)	0.0306 (1)
C2*b*	0.5969 (3)	0.1665 (3)	−0.0361 (4)	0.0292 (1)
C3*a*	0.3248 (3)	0.3413 (3)	0.3518 (4)	0.0324 (1)
C3*b*	0.4934 (3)	0.1686 (3)	−0.1433 (3)	0.0274 (1)
C4*a*	0.2034 (4)	0.3005 (3)	0.0967 (3)	0.0333 (1)
C4*b*	0.3122 (3)	0.0879 (3)	−0.3750 (4)	0.0317 (1)
C5*a*	0.2363 (4)	0.3957 (3)	0.0581 (4)	0.0366 (1)
C5*b*	0.3089 (4)	0.0408 (3)	−0.5294 (4)	0.0359 (1)
C6*a*	0.1451 (4)	0.4147 (3)	−0.0422 (4)	0.0374 (1)
C6*b*	0.2113 (4)	0.0518 (3)	−0.6307 (4)	0.0412 (1)
C7*a*	0.0197 (3)	0.3378 (3)	--0.1035 (4)	0.0334 (1)
C7*b*	0.1148 (3)	0.1101 (3)	−0.5802 (4)	0.0367 (1)

C8*a*	−0.0139 (4)	0.2437 (4)	−0.0641 (4)	0.0452 (1)
C8*b*	0.1161 (4)	0.1561 (4)	−0.4266 (4)	0.0470 (1)
C9*a*	0.0790 (4)	0.2244 (4)	0.0363 (4)	0.0447 (1)
C9*b*	0.2143 (4)	0.1434 (4)	−0.3250 (4)	0.0432 (1)
C10*a*	0.5026 (3)	0.2555 (3)	0.4382 (4)	0.0346 (1)
C10*b*	0.6352 (3)	0.0619 (3)	−0.0336 (4)	0.0311 (1)
C11*a*	−0.1979 (5)	0.2944 (5)	−0.2638 (6)	0.0650 (1)
C11*b*	−0.0782 (5)	0.1765 (5)	−0.6446 (7)	0.0681 (1)
O1*W*	0.0181 (3)	0.4662 (3)	0.3309 (4)	0.0612 (1)

Table 2. *Selected geometric parameters (Å, °)*

O1*a*—C1*a*	1.260 (4)	C1*a*—C2*a*	1.424 (4)
O1*b*—C1*b*	1.249 (4)	C1*b*—C2*b*	1.427 (5)
O2*a*—C7*a*	1.378 (4)	C2*a*—C3*a*	1.396 (4)
O2*b*—C7*b*	1.365 (4)	C2*b*—C3*b*	1.398 (4)
O2*a*—C11*a*	1.433 (5)	C2*a*—C10*a*	1.405 (5)
O2*b*—C11*b*	1.418 (6)	C2*b*—C10*b*	1.412 (5)
N1*a*—N2*a*	1.397 (4)	C4*a*—C5*a*	1.373 (5)
N1*b*—N2*b*	1.412 (4)	C4*b*—C5*b*	1.378 (4)
N1*a*—C3*a*	1.343 (4)	C4*a*—C9*a*	1.371 (5)
N1*b*—C3*b*	1.348 (5)	C4*b*—C9*b*	1.373 (5)
N2*a*—C1*a*	1.357 (4)	C5*a*—C6*a*	1.374 (5)
N2*b*—C1*b*	1.380 (4)	C5*b*—C6*b*	1.372 (5)
N3*a*—C3*a*	1.341 (4)	C6*a*—C7*a*	1.383 (5)
N3*b*—C3*b*	1.345 (4)	C6*b*—C7*b*	1.380 (5)
N3*a*—C4*a*	1.441 (4)	C7*a*—C8*a*	1.367 (5)
N3*b*—C4*b*	1.432 (4)	C7*b*—C8*b*	1.375 (5)
N4*a*—C10*a*	1.146 (4)	C8*a*—C9*a*	1.388 (5)
N4*b*—C10*b*	1.134 (4)	C8*b*—C9*b*	1.388 (5)
C7*a*—O2*a*—C11*a*	118.4 (3)	C3*b*—N3*b*—C4*b*	124.3 (3)
C7*b*—O2*b*—C11*b*	118.5 (3)	N2*a*—C1*a*—C2*a*	105.3 (3)
N2*a*—N1*a*—C3*a*	107.1 (3)	N2*b*—C1*b*—C2*b*	106.1 (3)
N2*b*—N1*b*—C3*b*	107.9 (3)	C1*a*—C2*a*—C3*a*	107.6 (3)
N1*a*—N2*a*—C1*a*	110.7 (3)	C1*b*—C2*b*—C3*b*	107.4 (3)
N1*b*—N2*b*—C1*b*	108.7 (3)	N1*b*—C3*b*—C2*b*	109.1 (3)
C3*a*—N3*a*—C4*a*	121.6 (3)	N1*a*—C3*a*—C2*a*	108.9 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*
N1*a*—H1*a*···O1*W*	0.97 (4)	1.78 (4)	2.743 (6)
N1*b*—H1*b*···O1*a*^{i}	0.97 (3)	1.81 (4)	2.752 (5)
N2*a*—H2*a*···O1*b*^{ii}	0.85 (3)	1.96 (3)	2.794 (5)
N2*b*—H2*b*···O1*a*^{ii}	0.93 (4)	1.90 (4)	2.820 (5)
N3*a*—H3*a*···N4*b*^{iii}	0.89 (4)	2.16 (4)	3.026 (7)
N3*b*—H3*b*···N4*a*^{iii}	0.93 (4)	2.16 (4)	3.041 (7)
O1*W*—H11*W*···O1*b*^{iv}	1.07 (7)	1.96 (7)	2.894 (6)
O1*W*—H12*W*···O2*a*^{v}	0.88 (6)	1.97 (6)	2.828 (5)

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, -y, -z$; (iv) $x-1, y, z$; (v) $-x, 1-y, -z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Dicyano-4′,5′-ethylenedithiotetrathiafulvalene (CNET)†: a New Unsymmetrical TTF Derivative

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Abstract

The molecule of the title compound, $C_{10}H_4N_2S_6$, is nearly planar except for the ethylene group. Intermolecular S···S interactions are found along the *a* axis in the crystal structure.

Comment

Various chemical modifications of TTF (tetrathiafulvalene) have been investigated because their radical-

† Alternative nomenclature: 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-1,3-dithiole-4,5-dicarbonitrile.