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Isolated molecules in 2-ethylsulfanyl-7-methyl-4-(4-methylphenyl)pyrazolo-[1,5-*a*][1,3,5]triazine and hydrogen-bonded sheets of $R_2^2(10)$, $R_2^2(16)$, $R_4^4(22)$ and $R_4^4(24)$ rings in 2-ethylsulfanyl-7-methyl-4-(4-nitrophenyl)-pyrazolo[1,5-*a*][1,3,5]triazine

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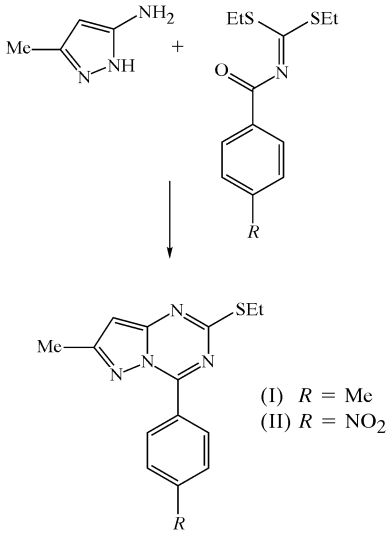
In each of 2-ethylsulfanyl-7-methyl-4-(4-methylphenyl)pyrazolo[1,5-*a*][1,3,5]triazine, $C_{15}H_{16}N_4S$, (I), and 2-ethylsulfanyl-7-methyl-4-(4-nitrophenyl)pyrazolo[1,5-*a*][1,3,5]triazine, $C_{14}H_{13}N_5O_2S$, (II), there is significant bond fixation in the heterocyclic component. While there are no direction-specific intermolecular interactions in the structure of (I), the molecules of (II) are linked by a combination of C—H···O and C—H···S hydrogen bonds into sheets containing four types of ring, all centrosymmetric.

Comment

Pyrazolo[1,5-*a*][1,3,5]triazines have attracted considerable interest from the medicinal chemistry community because of their wide range of biological activities (De Zwart *et al.*, 1999; He *et al.*, 2000). Derivatives containing such ring systems have been synthesized from 5-aminopyrazoles and an appropriate bis-electrophilic reagent (Strohmeyer *et al.*, 1985; Ried & Aboul-Fetouh, 1988; Elgemeie *et al.*, 2001). We report here the structures of two closely related pyrazolo[1,5-*a*]-1,3,5-triazines, *viz.* 2-ethylsulfanyl-7-methyl-4-(4-methylphenyl)-pyrazolo[1,5-*a*][1,3,5]triazine, (I) (Fig. 1), and 2-ethylsulfanyl-7-methyl-4-(4-nitrophenyl)pyrazolo[1,5-*a*][1,3,5]triazine, (II) (Fig. 2), which were obtained from the reactions of 5-amino-3-methylpyrazole with the appropriate 4-substituted *S*,*S*-diethyl aroyliminodithiocarbonates.

In the fused heterobicyclic components of the molecules, the corresponding bond lengths for compounds (I) and (II) are very similar (Table 1), and they show a number of interesting features. Firstly, the N1—C2 and N3—C4 bonds are significantly shorter than the C2—N3, C4—N5 and C9—N1



bonds, while the cross-ring bond N5—C9 is by far the longest of the C—N bonds in this system; secondly, the C8—C9 bond is significantly shorter than the C7—C8 bond. These observations provide evidence for a significant measure of bond fixation within this ring system. In each of (I) and (II), the pendent aryl ring is almost coplanar with the heterocyclic system, and this configuration may be associated with the presence, in each compound, of an intramolecular C—H···N contact to pyrazole atom N6. In (II), the nitro group is nearly coplanar with the aryl ring, with a dihedral angle between the

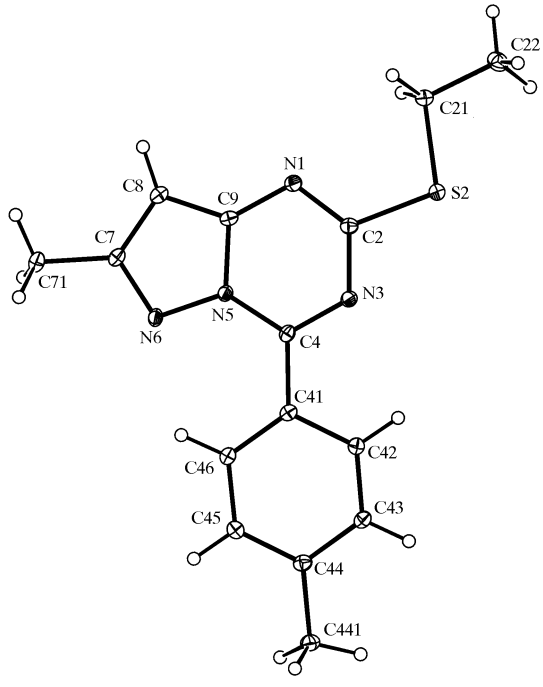


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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planes of the aryl group and the C—NO_2 unit of only 14.3 (2)°. However, the conformation of the ethylsulfanyl substituent differs between compounds (I) and (II), with the C21—C22 bond antiperiplanar to C2—S2 in (I) but synclinal in (II) (Table 1); the exocyclic C2—S2 distances are significantly different in the two compounds, possibly as a consequence of the conformational difference, although the S2—C21 distances are not significantly different.

There are no direction-specific intermolecular interactions in the structure of (I). However, the molecules of (II) are linked by two independent C—H···O hydrogen bonds (Table 2) into chains of edge-fused rings, which are themselves further linked, albeit rather weakly, by a single C—H···S hydrogen bond.

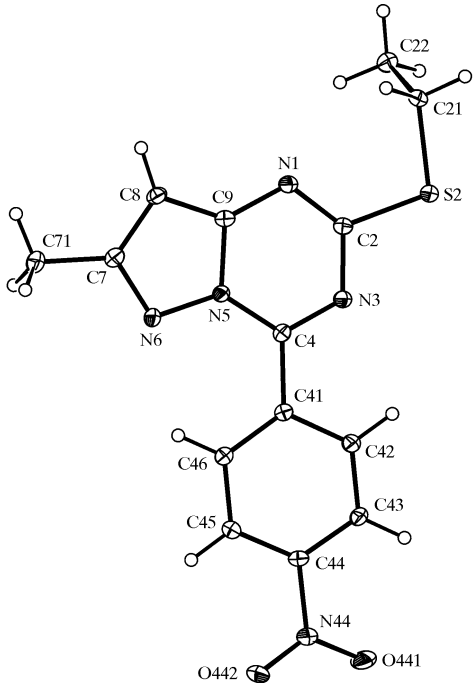

Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

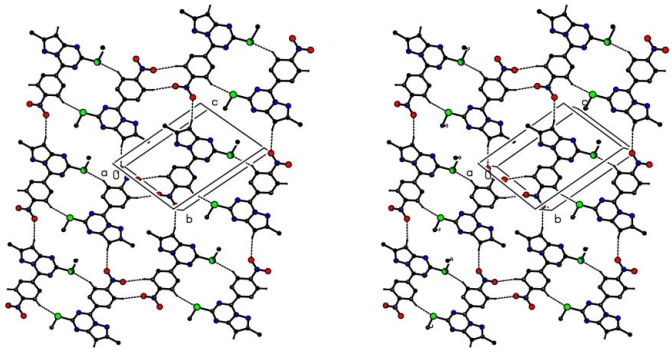

Figure 3
A stereoview of part of the crystal structure of (II), showing the formation of a (2$1\bar{1}$) sheet built from four types of ring. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Pyrazole atom C8 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to nitro atom O441 in the molecule at (1 + *x*, −1 + *y*, 1 + *z*), so generating by translation a *C*(11) (Bernstein *et al.*, 1995) chain running parallel to the [1$\bar{1}$1] direction. There are two chains of this type passing through each unit cell, related by inversion and hence antiparallel to one another, and such pairs of antiparallel chains are linked by the second C—H···O hydrogen bond. Aryl atom C45 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to nitro atom O442 in the molecule at (1 − *x*, 1 − *y*, −*z*), so generating by translation and inversion a chain of edge-fused $R_2^2(10)$ and $R_4^4(24)$ rings running along [1$\bar{1}$1] (Fig. 3). Finally, aryl atom C43 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom S2 in the molecule at (1 − *x*, 2 − *y*, 1 − *z*), so linking the [1$\bar{1}$1] chains into (2$1\bar{1}$) sheets built from four types of ring, *viz.* $R_2^2(10)$, $R_2^2(16)$, $R_4^4(22)$ and $R_4^4(24)$, all of them centrosymmetric (Fig. 3).

Experimental

A solution of 5-amino-3-methylpyrazole (0.034 mol) and the appropriate *S*,*S*-diethyl aroyliminodithiocarbonate (0.034 mol) in dimethylformamide (2 ml) was heated under reflux until the reaction was complete. The solid products were precipitated by addition of cold water to the reaction mixture, collected by filtration and purified by column chromatography on silica gel, using a mixture of hexanes/ethyl acetate (4:1 *v*/*v*) as eluant. Compound (I) was obtained after heating for 1 h, and evaporation of the solution in hexanes/ethyl acetate (4:1 *v*/*v*) provided crystals suitable for single-crystal X-ray diffraction (yield 63%, m.p. 388 K). Compound (II) was obtained after heating for 30 min; recrystallization from absolute ethanol provided crystals suitable for single-crystal X-ray diffraction (yield 50%, m.p. 393 K).

Compound (I)

Crystal data

$C_{15}H_{16}N_4S$
M_r = 284.38
Monoclinic, $P2_1/c$
a = 16.0941 (5) Å
b = 5.5573 (2) Å
c = 15.2495 (5) Å
β = 96.2994 (17)°
V = 1355.68 (8) Å^3
Z = 4
D_x = 1.393 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3092 reflections
θ = 3.8–27.5°
μ = 0.23 mm^{-1}
T = 120 (2) K
Lath, yellow
0.54 × 0.32 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.884, T_{max} = 0.977
14663 measured reflections
3092 independent reflections
2458 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.5°
h = −20 → 20
k = −7 → 7
l = −17 → 19

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.124
S = 1.05
3092 reflections
184 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.834P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for compounds (I) and (II).

	(I)	(II)
N1—C2	1.316 (2)	1.310 (2)
C2—N3	1.360 (2)	1.370 (2)
N3—C4	1.317 (2)	1.310 (2)
C4—N5	1.374 (2)	1.370 (2)
N5—N6	1.376 (2)	1.375 (2)
N6—C7	1.339 (2)	1.341 (2)
C7—C8	1.402 (3)	1.403 (3)
C8—C9	1.376 (3)	1.371 (2)
C9—N1	1.361 (2)	1.360 (2)
N5—C9	1.401 (2)	1.409 (2)
C2—S2	1.7499 (19)	1.7432 (18)
S2—C21	1.8099 (19)	1.8063 (18)
C2—S2—C21—C22	179.01 (13)	78.57 (15)
N3—C4—C41—C42	2.5 (3)	−1.1 (2)
C43—C44—N44—O441	–	14.5 (2)

Compound (II)

Crystal data

$C_{14}H_{13}N_5O_2S$
M_r = 315.35
Triclinic, $P\overline{1}$
a = 7.9401 (2) Å
b = 8.8642 (3) Å
c = 11.3717 (4) Å
α = 68.7710 (17)°
β = 85.792 (2)°
γ = 72.214 (2)°
V = 709.77 (4) Å^3
Z = 2
D_x = 1.476 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3255 reflections
θ = 3.2–27.6°
μ = 0.24 mm^{-1}
T = 120 (2) K
Plate, yellow
0.24 × 0.16 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.939, T_{max} = 0.990
16065 measured reflections
3255 independent reflections
2475 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.6°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.106
S = 1.06
3255 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2934P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

For (I), the space group $P2_1/c$ was uniquely assigned from the systematic absences; crystals of (II) are triclinic, and the space group $P\overline{1}$ was selected and subsequently confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 (CH), 0.98 (CH_3) or 0.99 Å (CH_2), and with U_{iso}(H) values of 1.2U_{eq}(C), or 1.5U_{eq}(C) for the methyl groups.

Table 2
Hydrogen bonds and short intramolecular contacts (Å, °) for compounds (I) and (II).

Compound	D—H···A	D—H	H···A	D···A	D—H···A
(I)	C46—H46···N6	0.95	2.24	2.909 (2)	127
(II)	C46—H46···N6	0.95	2.26	2.929 (2)	127
	C8—H8···O441^{i}	0.95	2.53	3.444 (2)	161
	C43—H43···S2^{ii}	0.95	2.84	3.453 (2)	123
	C45—H45···O442^{iii}	0.95	2.50	3.437 (2)	169

Symmetry codes: (i) $1+x, -1+y, 1+z$; (ii) $1-x, 2-y, 1-z$; (iii) $1-x, 1-y, -z$.

For both compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1896). Services for accessing these data are described at the back of the journal.

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