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A simple hydrogen-bonded chain in (3*Z*)-3-{1-[(5-phenyl-1*H*-pyrazol-3-yl)amino]ethylidene}-4,5-dihydrofuran-2(3*H*)-one, and a hydrogen-bonded ribbon of centrosymmetric rings in the self-assembled adduct (3*Z*)-3-{1-[(5-methyl-1*H*-pyrazol-3-yl)amino]ethylidene}-4,5-dihydrofuran-2(3*H*)-one–6-(2-hydroxyethyl)-2,5-dimethylpyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one (1/1)

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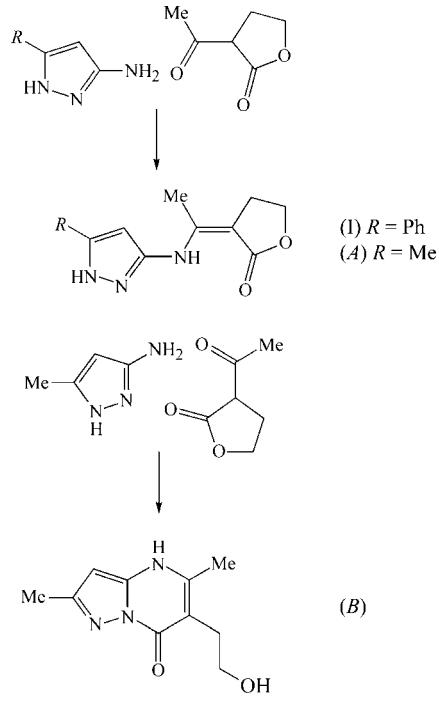
(3*Z*)-3-{1-[(5-Phenyl-1*H*-pyrazol-3-yl)amino]ethylidene}-4,5-dihydrofuran-2(3*H*)-one, $C_{15}H_{15}N_3O_2$, (I), and the stoichiometric adduct (3*Z*)-3-{1-[(5-methyl-1*H*-pyrazol-3-yl)amino]-ethylidene}-4,5-dihydrofuran-2(3*H*)-one–6-(2-hydroxyethyl)-2,5-dimethylpyrazolo[1,5-*a*]pyrimidin-7(4*H*)-one (1/1), $C_{10}H_{13}N_3O_2{\cdot}C_{10}H_{13}N_3O_2$, (II), in which the two components have the same composition but different constitutions, are formed in the reactions of 2-acetyl-4-butyrolactone with 5-amino-3-phenyl-1*H*-pyrazole and 5-amino-3-methyl-1*H*-pyrazole, respectively. In each compound, the furanone component contains an intramolecular N—H···O hydrogen bond. The molecules of (I) are linked into a chain by a single intermolecular N—H···O hydrogen bond, while in (II), a combination of one O—H···N hydrogen bond, within the selected asymmetric unit, and two N—H···O hydrogen bonds link the molecular components into a ribbon containing alternating centrosymmetric $R_4^4(20)$ and $R_6^6(22)$ rings.

Comment

The condensation reactions between substituted aminopyrazoles and dicarbonyl compounds provide a potentially very versatile route for the synthesis of new fused heterocyclic compounds with precisely defined regiochemistry (Portilla *et al.*, 2008), and fused pyrazole derivatives are potentially valuable for drug and pesticide applications (Elguero, 1984,1996). Here, we report the structures of the two title compounds, (I) and (II) (Figs. 1 and 2), which result from the condensation reactions between 2-acetyl-4-butyrolactone and two 5-amino-1*H*-pyrazoles carrying different hydrocarbyl substituents at position 3 (see reaction scheme).



(II)

The reaction between equimolar quantities of the lactone and 5-amino-3-phenyl-1*H*-pyrazole provides (3*Z*)-3-{1-[(5-phenyl-1*H*-pyrazol-3-yl)amino]ethylidene}-4,5-dihydrofuran-2(3*H*)-one, (I), which apparently results from a simple condensation involving only the 2-acetyl substituent in the lactone reagent, to form a product in which the lactone ring survives intact (see reaction scheme). By contrast, the corresponding reaction between the same lactone reagent and 5-amino-3-methyl-1*H*-pyrazole proceeds along two different reaction pathways. One of these pathways is entirely analogous to that which forms compound (I), leading to the product denoted (*A*) in the reaction scheme. The second pathway involves both carbonyl functions in the lactone component, which itself undergoes ring opening, so that this pathway is indeed a cyclocondensation reaction giving a fused heterocyclic system in the product denoted (*B*) in the reaction

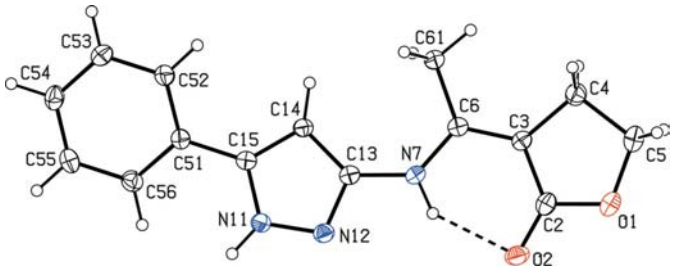


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme and the intramolecular hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

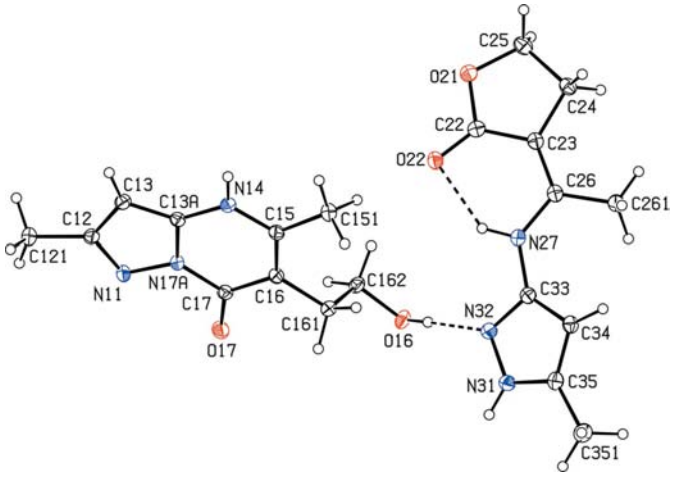
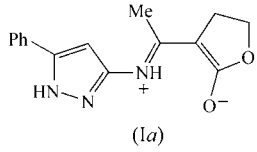


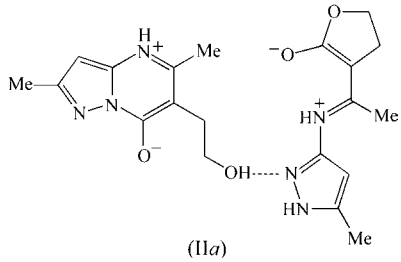
Figure 2
The independent molecular components of compound (II), showing the atom-labelling scheme and the hydrogen bonds within the asymmetric unit (dashed line). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

scheme. Product (II), which crystallizes from the reaction between 5-amino-3-methyl-1*H*-pyrazole and the lactone, is a 1:1 hydrogen-bonded adduct formed by the primary products (*A*) and (*B*), which are, in fact, isomeric with one another despite their very different constitutions.

Within the molecule of compound (I), the C2—O2 and C3—C6 bonds (Table 1) are both long for their types [mean values (Allen *et al.*, 1987) = 1.201 and 1.340 Å, respectively, upper quartile values = 1.206 and 1.348 Å, respectively] and the C2—C3 bond is short for its type (mean value = 1.464 Å, lower quartile value = 1.453 Å), while the N7—C6 bond is significantly shorter than the N7—C13 bond. These values provide evidence for electronic polarization in the vinylogous amide fragment of (I), indicating that the form (I*a*) is a significant contributor to the overall electronic structure. A similar pattern of distances is found in component (*A*) of compound (II) (Table 3), but the deviations from the expected values are all somewhat smaller in (II), indicative of a lesser degree of electronic polarization in this component. A similar pattern is found also in the vinylogous amide fragment in component (*B*) of (II), indicating a contribution from the form (II*a*). Consistent with this observation concerning component (*B*) of (II), the C12—C13 and C13—C13*A* bonds in (II) differ in length by almost 0.04 Å, while the corresponding differences in (I) and in component (*A*) of (II) are no more than half of this value. In addition, the C13*A*—N17*A* bond in (II) is rather longer than the corresponding bonds in the unfused pyrazole rings of both (I) and (II), indicating stronger bond fixation in the fused pyrazole ring than in either of the unfused pyrazole rings.



(I*a*)



(II*a*)

The molecules of (I) contain an intramolecular N—H···O hydrogen bond (Table 2, Fig. 1) forming an *S*(6) motif (Bernstein *et al.*, 1995), and molecules related by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ are linked into chains by a second N—H···O hydrogen bond to form an $S(6)C(9)C_2^1(7)$ chain of rings running parallel to the [010] direction (Fig. 3). Two chains of

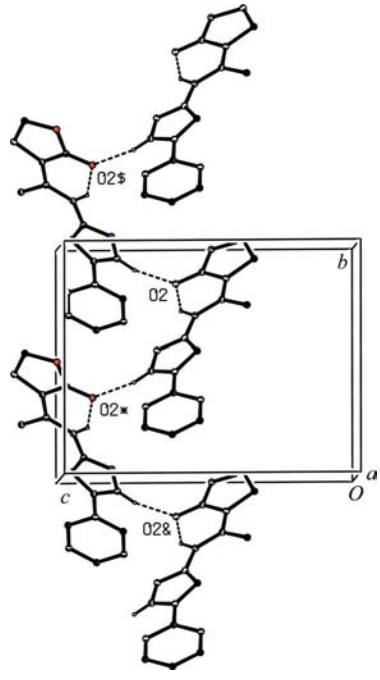


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings running parallel to [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Dashed lines indicate hydrogen bonds. Atoms marked with an asterisk (*), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, -1 + y, z)$, respectively.

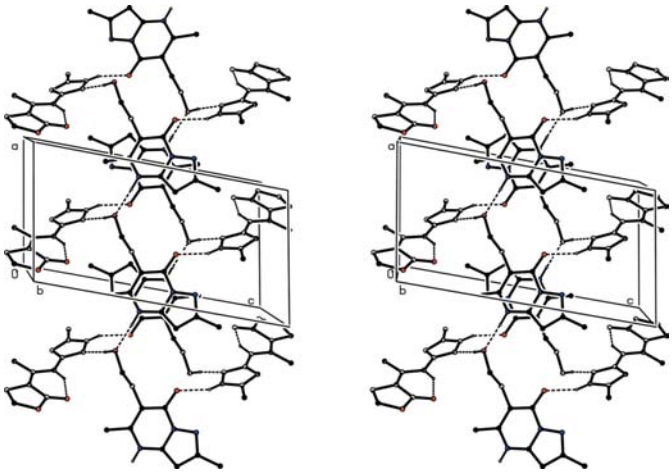


Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded ribbon parallel to [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Dashed lines indicate hydrogen bonds.

this type, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent chains. In particular, there are neither C—H···π(arene) hydrogen bonds nor aromatic π–π stacking interactions in the structure of (I).

Within the selected asymmetric unit of (II) (Fig. 2), the two components are linked by a fairly short and almost linear O—H···N hydrogen bond (Table 4), and there is also an intramolecular N—H···O hydrogen bond, analogous to that in (I). Two further N—H···O hydrogen bonds then link the bimolecular aggregates into a ribbon containing two types of centrosymmetric ring and running parallel to the [100] direction. Within the ribbon, $R_4^4(20)$ rings centred at $(n+\frac{1}{2},\frac{1}{2},\frac{1}{2})$, where n represents an integer, alternate with $R_6^6(22)$ rings centred at $(n,\frac{1}{2},\frac{1}{2})$, where n again represents an integer (Fig. 4).

Experimental

For the synthesis of compound (I), a mixture of 2-acetyl-4-butyrolactone (1 mmol), 5-amino-3-phenyl-1*H*-pyrazole (1 mmol) and 4-toluenesulfonic acid (0.01 mmol) in ethanol (15 ml) was heated under reflux with magnetic stirring for 18 h. The mixture was cooled to ambient temperature and the solvent was removed under reduced pressure. The resulting solid product was recrystallized from dimethylformamide to yield (I) as colourless crystals (yield 63%, m.p. 595–596 K). MS (70 eV) *m*/*z* (%): 269 (5, M^+), 251 (35), 104 (25), 18 (100).

For the synthesis of compound (II), a mixture of 2-acetyl-4-butyrolactone (1 mmol), 5-amino-3-methyl-1*H*-pyrazole (1 mmol) and 4-toluenesulfonic acid (0.01 mmol) in ethanol (15 ml) was heated under reflux with magnetic stirring for 23 h. The reaction mixture was cooled to ambient temperature and the solvent was removed under reduced pressure. The resulting solid product was recrystallized from dimethylformamide to yield (II) as colourless crystals (yield 48%, m.p. 493–494 K). MS (70 eV) *m*/*z* (%): 207 (6, M^+), 189 (23), 152 (8), 86 (41), 43 (100).

Table 1
Selected bond lengths (Å) for (I).

C2—O2	1.232 (3)	N11—N12	1.341 (2)
C2—C3	1.413 (3)	N12—C13	1.324 (3)
C3—C6	1.369 (3)	C13—C14	1.394 (3)
C6—N7	1.338 (3)	C14—C15	1.371 (3)
N7—C13	1.380 (3)	C15—N11	1.340 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O2	0.88	1.97	2.709 (2)	141
N11—H11···O2^{i}	0.88	1.97	2.784 (2)	154

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Compound (I)

Crystal data

$C_{15}H_{15}N_3O_2$
M_r = 269.30
Monoclinic, $P2_1/c$
a = 10.4969 (17) Å
b = 9.8550 (9) Å
c = 12.6739 (16) Å
β = 99.883 (9)°
V = 1291.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 K
0.39 × 0.25 × 0.14 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.964, T_{max} = 0.987
19109 measured reflections
2536 independent reflections
1704 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.128
S = 1.07
2536 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Compound (II)

Crystal data

$C_{10}H_{13}N_3O_2{\cdot}C_{10}H_{13}N_3O_2$
M_r = 414.46
Triclinic, $P\overline{1}$
a = 8.0402 (11) Å
b = 8.2025 (17) Å
c = 15.348 (3) Å
α = 91.999 (14)°
β = 99.785 (12)°
γ = 99.172 (15)°
V = 982.7 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 K
0.38 × 0.23 × 0.16 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.963, T_{max} = 0.984
21688 measured reflections
3857 independent reflections
2739 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.123
S = 1.07
3857 reflections
275 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

N11—C12	1.325 (2)	C22—O22	1.221 (2)
C12—C13	1.399 (3)	C22—C23	1.429 (3)
C13—C13*A*	1.361 (3)	C23—C26	1.356 (3)
C13*A*—N14	1.351 (2)	C26—N27	1.357 (2)
N14—C15	1.351 (2)	N27—C33	1.386 (2)
C15—C16	1.362 (3)	N31—N32	1.351 (2)
C16—C17	1.422 (3)	N32—C33	1.329 (3)
C17—N17*A*	1.389 (2)	C33—C34	1.389 (3)
N17*A*—N11	1.364 (2)	C34—C35	1.374 (3)
C13*A*—N17*A*	1.365 (2)	C35—N31	1.331 (3)
C17—O17	1.229 (2)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O16—H16···N32	0.86	1.93	2.784 (2)	175
N27—H27···O22	0.88	1.99	2.712 (2)	139
N14—H14···O16^{i}	0.88	1.86	2.736 (2)	172
N31—H31···O17^{ii}	0.88	1.93	2.740 (2)	153

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

All H atoms were located in difference maps. H atoms bonded to C or N atoms were then treated as riding in geometrically idealized positions, with C—H = 0.95 (aromatic or pyrazole), 0.98 (CH_3) or 0.99 Å (CH_2) and N—H = 0.88 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C or N atoms. The H atom bonded to an O atom in compound (II) was permitted to ride at the position deduced from the difference maps, with $U_{iso}(H) = 1.5U_{eq}(O)$, giving an O—H distance of 0.86 Å.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3210). Services for accessing these data are described at the back of the journal.

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