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2-Cyano-*N*-(2,6-dimethoxypyrimidin-4-yl)-3-[4-(dimethylamino)phenyl]-acrylamide and dimethylammonium 6-cyano-1,3-dimethyl-2,4,5-trioxo-1,2,3,4,5,8-hexahydropyrido[2,3-*d*]-pyrimidin-8-ide: a π-stacked dimer and a hydrogen-bonded ribbon containing three types of ring

Jairo Quiroga,[a] Jaime Gálvez,[a] Michael B. Hursthouse,[b] Justo Cobo[c] and Christopher Glidewell[d]*

[a]Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England, [c]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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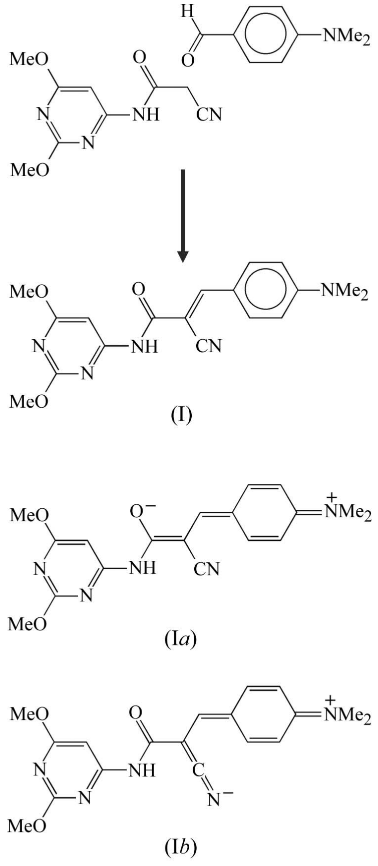
The bond distances in 2-cyano-*N*-(2,6-dimethoxypyrimidin-4-yl)-3-[4-(dimethylamino)phenyl]acrylamide, $C_{18}H_{19}N_5O_3$, (I), and in the anionic component of the salt dimethylammonium 6-cyano-1,3-dimethyl-2,4,5-trioxo-1,2,3,4,5,8-hexahydropyrido[2,3-*d*]pyrimidin-8-ide, $C_2H_8N_2^+\cdot C_{10}H_7N_4O_3^-$, (II), provide evidence for the occurrence of electronic polarization. There are no hydrogen bonds in the structure of (I), instead pairs of molecules are linked into centrosymmetric dimers by a single π–π stacking interaction. In (II), a combination of a two-centre N—H···O hydrogen bond, a three-centre N—H···(O)$_2$ hydrogen bond, together utilizing all three O atoms, and a two-centre C—H···N hydrogen bond, link the components into a ribbon containing $R^2_1(6)$, $R^2_2(10)$ and $R^6_6(30)$ rings.

Comment

We report here the structures of the title compounds, (I) and (II) (Figs. 1 and 2), which result from the reactions of cyanoacetylpyrimidine derivatives with, respectively, 4-(dimethylamino)benzaldehyde (Quiroga *et al.*, 2009; see scheme 1) and dimethylformamide dimethylacetal (see scheme 2). The use of 5-cyanoacetylpyrimidines as intermediates for the synthesis of substituted pyrido[2,3-*d*]pyrimidin-5-ones has recently been described (Quiroga *et al.*, 2009), and compounds (I) and (II), were both synthesized using variations of the recently reported procedure.

Within the molecule of (I) (Fig. 1), the spacer unit linking the two rings adopts an all-*trans* configuration which is nearly planar, while the two rings are each twisted out of this plane by less than 10°, as shown by the leading torsion angles (Table 1). Similarly, the C atoms of the methoxy groups are almost coplanar with the adjacent pyrimidine ring, with deviations from the ring plane of 0.071 (2) Å for atom C21 and 0.195 (2) Å for atom C61, although the spatial disposition of these groups differs from that originally suggested (Quiroga *et al.*, 2009).



Scheme1

The bond distances in the molecule of (I) show some values which are worthy of comment (Table 1). In the C51–C56 aryl ring, the two bonds C52—C53 and C55—C56 are significantly shorter than the other four bonds; the exocyclic C54—N54 bond is somewhat short for its type [mean value (Allen *et al.*, 1987) = 1.371 Å]; the C45—C51 bond is very short for its type (mean value = 1.470 Å, lower quartile value = 1.463 Å), while the C43—C45 bond is long for its type (mean value = 1.326 Å, upper quartile value = 1.334 Å). Although the C42—C43 and C42—O42 bonds have lengths typical of their types, the C43—C44 bond is shorter than those found in a series of analogous nitriles where electronic conjugation is not possible [mean value = 1.442 (4) Å; Cobo *et al.*, 2005, 2006, 2009] and the C44—N44 bond is correspondingly longer [mean value =

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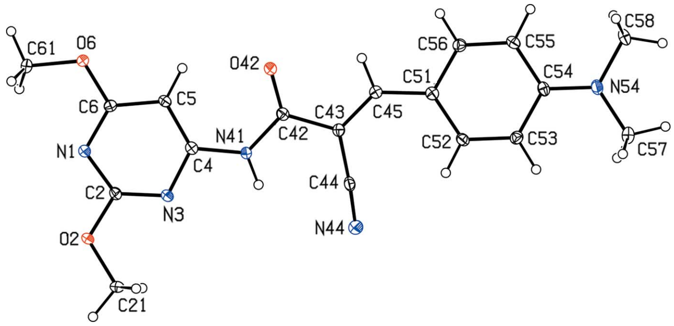
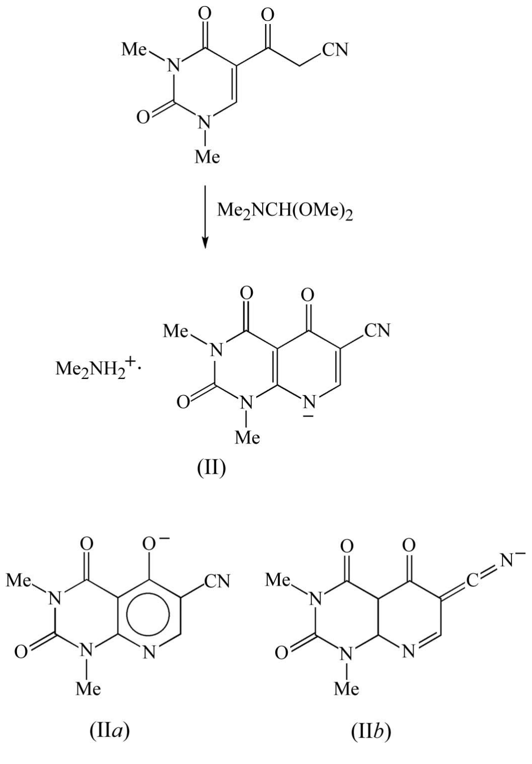


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

1.130 (4) Å]. Thus, within the spacer unit, the bond-length anomalies are concentrated in the carbonitrile fragment, rather than in the carbonyl fragment and its adjacent C—C bonds. Taken as a whole, the bond distances in (I) indicate that form (I*a*) (see scheme 1), which is intuitively the more obvious of the polarized forms, probably makes only a very small contribution to the overall electronic structure, while form (I*b*) is a significant contributor, in addition to the classical unpolarized form (I).



Scheme 2

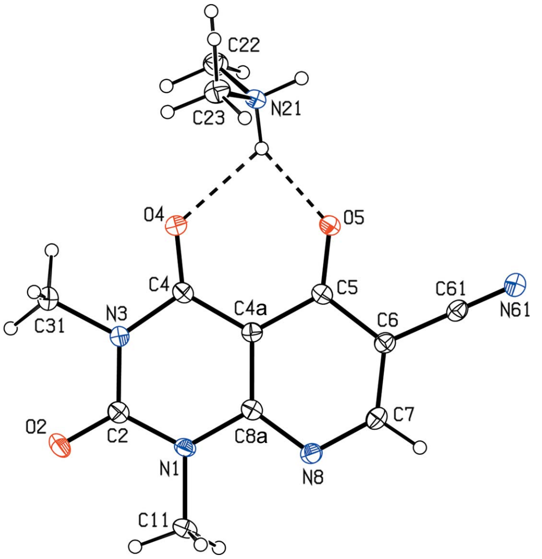


Figure 2
The independent components of (II), showing the atom-labelling scheme and the three-centre N—H···(O)$_2$ hydrogen bond (dashed lines) linking the ions within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

In the anion of compound (II) (Fig. 2), it is striking that, while the C2—O2 and C4—O4 distances are identical and typical of their type, the C5—O5 distance is significantly longer (Table 2). As found for the analogous bonds in (I), the C6—C61 bond in (II) is slightly short for its type and C61—N61 is slightly long. Thus, forms (II*a*) and, to a lesser extent, (II*b*) are contributors to the overall electronic structure, in addition to the simple form (II) (see second scheme).

Despite the polarization of the electronic structure in (I), neither atom O42 nor N44 acts as a hydrogen-bond acceptor. Indeed, there are no hydrogen bonds of any kind in the crystal structure of (I). In particular, the N—H unit does not act as a

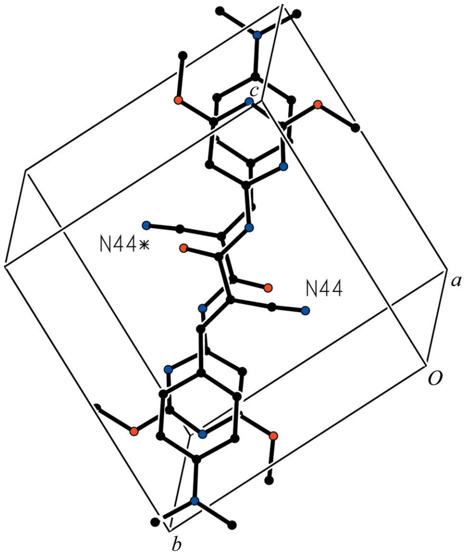


Figure 3
Part of the crystal structure of (I), showing the formation of a centrosymmetric π-stacked dimer. For the sake of clarity, H atoms have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(1 - x, 1 - y, 1 - z)$.

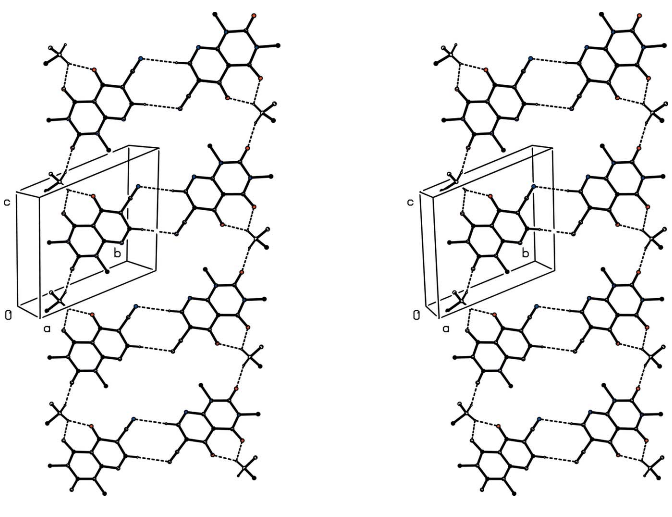
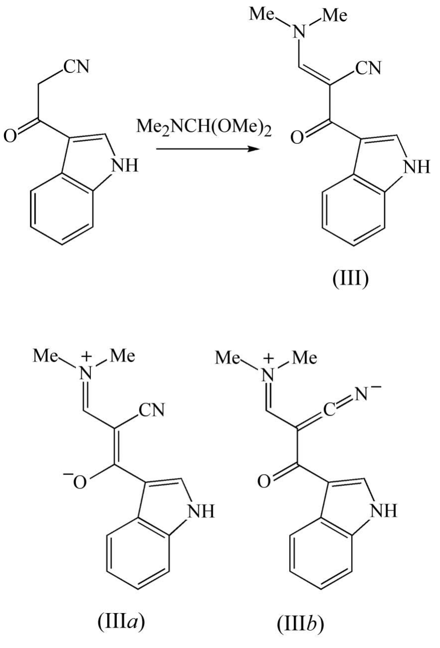


Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded ribbon running parallel to [001] and containing rings of $R_1^2(6)$, $R_2^2(10)$ and $R_6^6(30)$ types. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

hydrogen-bond donor, as the nearest potential hydrogen-bond acceptor is atom O42 in the molecule at $(1 - x, 1 - y, 1 - z)$ and the geometric parameters for this contact are $N41\cdots O42^{i}$ = 3.501 (2) Å, $H41\cdots O42^{i}$ = 3.51 Å and $N41—H41\cdots O42^{i}$ = 82° [symmetry code: (i) $1 - x, 1\ y, 1 - z$]. No N—H$\cdots\pi$ or C—H$\cdots\pi$ hydrogen bonds are present either. Instead, pairs of molecules related by inversion are linked into centrosymmetric dimers (Fig. 3) by a single π–π stacking interaction. The aryl ring of the molecule at (x, y, z) and the pyrimidine ring of the molecule at $(1 - x, 1 - y, 1 - z)$ make a dihedral angle of only 2.2 (2)°. The corresponding ring-centroid separation is 3.632 (2) Å and the interplanar spacing is *ca* 3.395 Å, with a ring-centroid offset of *ca* 1.29 Å. There are no direction-specific interactions between these dimers.



Scheme 3

In compound (II), the ionic components in the selected asymmetric unit are linked by a slightly asymmetric but nonetheless planar three-centre N—H$\cdots$(O)$_2$ hydrogen bond (Table 3 and Fig. 2), forming an $R_1^2(6)$ motif (Bernstein *et al.*, 1995). The shorter component of this three-centre system involves atom O5 as the acceptor and, because of the polarization in form (II*a*), this stronger component could be regarded as a charge-assisted hydrogen bond (Gilli *et al.*, 1994). In addition, atom N21 in the cation at (x, y, z) acts as hydrogen-bond donor to atom O2 in the anion at $(x, y, 1 + z)$, and the combination of all the N—H$\cdots$O interactions generates a hydrogen-bonded $C_2^2(8)C_2^2(10)[R_1^2(6)]$ chain of rings (Fig. 4). Finally, a single C—H$\cdots$N hydrogen bond, which utilizes the nitrile N atom as the acceptor, links an antiparallel pair of chains of rings into a ribbon running parallel to the [001] direction in which $R_2^2(10)$ rings centred at $(1, 1, \frac{1}{2} + n)$, where n represents an integer, alternate with $R_6^6(30)$ rings centred at $(1, 1, n)$, where n again represents an integer (Fig. 4). There are no direction-specific interactions between adjacent ribbons.

The formation of the salt (II) in the reaction of dimethylformamide dimethylacetal with a cyanoacetylpyrimidine derivative may be contrasted with the reaction (Galvez *et al.*, 2008) of the same acetal with a cyanoacetylindole derivative to form the neutral compound, (III) (see scheme 3). Here, the intramolecular distances indicate that both of the polarized forms, (III*a*) and (III*b*), are significant contributors to the overall electronic structure. The formation of these compounds, and of (I), attests to the synthetic versatility of cyanoacetyl derivatives as intermediates for the synthesis of new heterocyclic compounds.

Experimental

For the synthesis of (I), a solution of 2-cyano-*N*-(2,6-dimethoxypyrimidin-4-yl)acetamide (1.0 mmol) and 4-(dimethylamino)benzaldehyde (1.0 mmol) in ethanol (10 ml) containing a catalytic quantity of sodium hydroxide (20% *w*/*v* aqueous solution, 5 drops) was stirred for 3 h at ambient temperature. The resulting precipitate was collected by filtration, washed with ethanol, and crystallized by slow evaporation, at ambient temperature and in air, of a solution in a mixture of dimethylformamide and ethanol (1:1, *v*/*v*) to give yellow crystals of (I) suitable for single-crystal X-ray diffraction (yield 76%, m.p. 526–527 K). MS (70 eV): 354 (17), 353 (76, M^{+}), 352 (16), 199 (65), 182 (100), 172 (20), 171 (58), 156 (12).

For the synthesis of compound (II), a solution of 3-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-3-oxopropanenitrile (1.9 mmol) and dimethylformamide dimethyl acetal (3.0 mmol) in toluene (5.3 ml) was heated at 393 K for 30 min. The resulting solid product was collected by filtration, washed and crystallized by slow evaporation, at ambient temperature and in air, of a solution in ethanol to give yellow crystals of (II) suitable for single-crystal X-ray diffraction (yield 70%, m.p. 532–534 K). MS (70 eV): 232 {$M^{+} - 45$ [HN(CH$_3$)$_2$]} (37), 204 (12), 120 (35).

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

C42—O42	1.2276 (18)	C51—C52	1.410 (2)
C42—C43	1.489 (2)	C52—C53	1.373 (2)
C43—C44	1.430 (2)	C53—C54	1.418 (2)
C44—N44	1.152 (2)	C54—C55	1.412 (2)
C43—C45	1.361 (2)	C55—C56	1.375 (2)
C45—C51	1.434 (2)	C56—C51	1.411 (2)
C54—N54	1.363 (2)		
N3—C4—N41—C42	−170.16 (13)	N1—C2—O2—C21	−178.19 (12)
C4—N41—C42—C43	−177.93 (13)	N1—C6—O6—C61	−4.43 (19)
N41—C42—C43—C45	178.81 (12)	C53—C54—N54—C57	−3.2 (2)
C42—C43—C45—C51	178.03 (15)	C53—C54—N54—C58	−178.89 (13)
C43—C45—C51—C52	−8.9 (3)		

Compound (I)

Crystal data

$C_{18}H_{19}N_5O_3$
M_r = 353.38
Triclinic, $P\overline{1}$
a = 7.9772 (2) Å
b = 10.0023 (4) Å
c = 10.8409 (5) Å
α = 93.693 (2)°
β = 93.562 (3)°
γ = 99.196 (2)°
V = 849.80 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 K
0.23 × 0.12 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.978, T_{max} = 0.988
15270 measured reflections
3350 independent reflections
2512 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.133
S = 1.04
3350 reflections
239 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Compound (II)

Crystal data

$C_2H_8N^+\cdot C_{10}H_7N_4O_3^-$
M_r = 277.29
Triclinic, $P\overline{1}$
a = 8.1520 (5) Å
b = 9.2984 (8) Å
c = 9.7299 (8) Å
α = 69.609 (3)°
β = 70.741 (4)°
γ = 79.447 (5)°
V = 650.69 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 K
0.12 × 0.05 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.988, T_{max} = 0.997
9719 measured reflections
2419 independent reflections
1538 reflections with $I > 2\sigma(I)$
R_{int} = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.194
S = 1.03
2419 reflections
185 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

N1—C2	1.368 (4)	N8—C8a	1.340 (4)
C2—N3	1.381 (4)	C8a—N1	1.393 (4)
N3—C4	1.401 (3)	C4a—C8a	1.408 (4)
C4—C4a	1.447 (4)	C2—O2	1.225 (3)
C4a—C5	1.449 (4)	C4—O4	1.225 (4)
C5—C6	1.444 (4)	C5—O5	1.258 (3)
C6—C7	1.379 (4)	C6—C61	1.438 (4)
C7—N8	1.346 (4)	C61—N61	1.151 (4)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O2$^{\rm i}$	0.92	1.88	2.735 (4)	153
N21—H21B···O4	0.92	2.12	2.757 (3)	126
N21—H21B···O5	0.92	1.89	2.699 (3)	146
C7—H7···N61$^{\rm ii}$	0.95	2.54	3.483 (4)	172

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

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.98 Å for methyl H atoms or 0.95 Å for aromatic, heteroaromatic and alkenyl H atoms, and an N—H distance of 0.88 Å for the N—H group in (I) or 0.92 Å for the ammonium N—H distances in (II), 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.

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: FA3211). Services for accessing these data are described at the back of the journal.

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