Fig. 3. A stereoscopic projection on the $bc$ plane displaying one layer of crystal packing. The tilt of the acridine molecules with respect to the PMDA molecules can be seen clearly.



Fig. 4. A schematic drawing of the packing and of the dipole orientations of the donors.

The 2:1 donor–acceptor complex can be appropriately characterized as a sandwich of one acceptor between two donor molecules, Fig. 3. A schematic drawing of the packing and of the dipole orientations is displayed in Fig. 4. The angle between the plane normals of the donor and acceptor molecules is $7 \cdot 3^{\circ}$. The average distance of an Ac atom (excluding H atoms) from the plane of the acceptor is $3 \cdot 434$ Å, which is approximately $0 \cdot 1$ Å greater than that in the 1:1 complex. The angle between the intrasandwich stack axis (as determined from the coordinates of the molecular centroids neglecting H atoms) and the plane of the acceptor molecule is $ca$ $25^{\circ}$.

Space-group symmetry ($e.g.$ the glide reflection operator) generates a second unit of the complex as
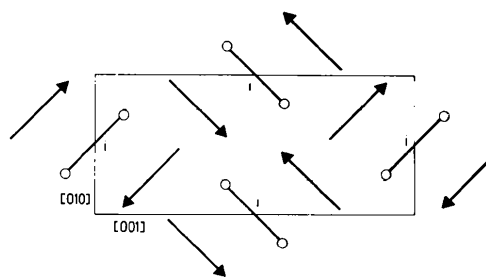
illustrated in Fig. 3. The angle between plane normals of symmetry-related donor molecules is $82 \cdot 3^{\circ}$, that between symmetry-related acceptor molecules is $67 \cdot 8^{\circ}$. The angle between the intrasandwich stack axis and the $b$ axis (the stack axis in the crystal) is $41^{\circ}$. Remarkably, the $\cdots DADADA \cdots$ sequence, typical for 1:1 complexes with weak charge-transfer interactions in the (electronic) ground state, is reduced to discrete $DAD$ units which display little overlap of $\pi$-orbitals with neighbouring units.

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# 2,2,8,9-Tetramethyl-1,2-dihydropurine-6-carboxamide

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**Abstract.** $C_{10}H_{15}N_5O$, $M_r = 221 \cdot 26$, monoclinic, $C2/c$, $a = 13 \cdot 900$ (4), $b = 8 \cdot 992$ (1), $c = 18 \cdot 091$ (7) Å, $\beta = 98 \cdot 98$ (2)$^{\circ}$, $V = 2233 \cdot 5$ Å$^3$, $Z = 8$, $D_x = 1 \cdot 32$ Mg m$^{-3}$, $F(000) = 944$, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 99$ mm$^{-1}$, $R = 0 \cdot 037$ for 1243 data with $I > 3\sigma$. The 1,2-dihydropurine ring system approaches planarity except for C(2) where the full ring conjugation found in purines is broken. The carbamoyl group is nearly

coplanar with the conjugated ring atoms and forms an internal hydrogen bond to N(7). An interpenetrating network of hydrogen bonds links dimers [N(1)···O(12$^i$) = 3·106 (3) Å] through N(3) and N(11).

**Introduction.** Orange-red crystals of the title compound (TDC) were synthesized as part of an investigation into the use of diaminomaleonitrile (DAMN) as a purine precursor (Booth & Proença, 1981). Spectroscopic examination of intermediates in the purine synthesis did not provide conclusive evidence of their structures and the present X-ray investigation was undertaken to elucidate the course of the synthetic route from DAMN to purines.

A crystal of TDC, not exceeding 0·3 mm maximum dimensions, was examined photographically with Cu $K\alpha$ radiation. Approximate cell parameters and the space group were determined prior to transfer to a CAD-4 diffractometer. Using graphite-monochromatized Mo $K\alpha$ radiation accurate cell parameters were determined on the diffractometer and the space group was confirmed. Intensities were collected for $\theta < 25°$ using $\omega/2\theta$ scans. Of the 1646 intensity

measurements of unique reflections made, 1243 had $I > 3\sigma$ and were used in the structure determination. Lorentz and polarization, but not absorption, corrections were applied. *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) was used to solve the phase problem, and the resulting $E$ map revealed all the non-H atoms. The atomic parameters of these atoms were refined anisotropically by full-matrix least squares with *SHELX* (Sheldrick, 1976) and a subsequent difference Fourier map revealed all the H atoms. The atomic coordinates and isotropic temperature factors of the H atoms were included in the refinement and the final $R$ was 0·037 [$R_w = 0·039$, $w = 0·9810/(\sigma^2 + 0·0015F^2)$]. Fluctuations on the final difference Fourier map did not exceed $\pm0·3$ e Å$^{-3}$.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and all computations were performed on the joint CDC 7600/ICL 1906A computer system of the University of Manchester Regional Computing Centre. Table 1* lists

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Table 1. *Fractional coordinates and isotropic vibrational parameters* (Å$^2$) *with e.s.d.'s in parentheses*

For non-H atoms, $U_{eq}$ values (Hamilton, 1959) are listed.

| | $x$ | $y$ | $z$ | $U_{eq}, U_{Iso}$ |
|---|---|---|---|---|
| N(1) | 0·5484 (1) | 0·4341 (2) | 0·6619 (1) | 0·0342 |
| C(2) | 0·6292 (1) | 0·3260 (2) | 0·6614 (1) | 0·0337 |
| N(3) | 0·6298 (1) | 0·2565 (2) | 0·5870 (1) | 0·0372 |
| C(4) | 0·5486 (2) | 0·2636 (2) | 0·5427 (1) | 0·0301 |
| C(5) | 0·4610 (1) | 0·3416 (2) | 0·5524 (1) | 0·0291 |
| C(6) | 0·4649 (1) | 0·4316 (2) | 0·6129 (1) | 0·0277 |
| N(7) | 0·3894 (1) | 0·3225 (2) | 0·4893 (1) | 0·0409 |
| C(8) | 0·4308 (2) | 0·2399 (2) | 0·4442 (1) | 0·0371 |
| N(9) | 0·5260 (1) | 0·2007 (2) | 0·4723 (1) | 0·0347 |
| C(10) | 0·3858 (1) | 0·5346 (2) | 0·6293 (1) | 0·0307 |
| N(11) | 0·3073 (1) | 0·5422 (2) | 0·5776 (1) | 0·0420 |
| O(12) | 0·3967 (1) | 0·6052 (2) | 0·6883 (1) | 0·0421 |
| C(13) | 0·6177 (3) | 0·2022 (3) | 0·7168 (2) | 0·0587 |
| C(14) | 0·7240 (2) | 0·4078 (4) | 0·6843 (2) | 0·0580 |
| C(15) | 0·5908 (2) | 0·1058 (3) | 0·4378 (2) | 0·0452 |
| C(16) | 0·3829 (2) | 0·1896 (4) | 0·3693 (2) | 0·0510 |
| H(11) | 0·554 (2) | 0·492 (3) | 0·700 (1) | 0·035 (6) |
| H(111) | 0·258 (2) | 0·602 (3) | 0·583 (1) | 0·053 (7) |
| H(112) | 0·301 (2) | 0·492 (4) | 0·536 (2) | 0·060 (8) |
| H(131) | 0·550 (3) | 0·148 (4) | 0·702 (2) | 0·101 (13) |
| H(132) | 0·672 (2) | 0·127 (4) | 0·718 (2) | 0·081 (10) |
| H(133) | 0·619 (2) | 0·245 (3) | 0·769 (2) | 0·064 (8) |
| H(141) | 0·725 (2) | 0·484 (4) | 0·644 (2) | 0·076 (10) |
| H(142) | 0·783 (2) | 0·336 (4) | 0·692 (2) | 0·070 (9) |
| H(143) | 0·727 (2) | 0·455 (3) | 0·731 (2) | 0·055 (7) |
| H(151) | 0·574 (2) | 0·111 (4) | 0·384 (2) | 0·081 (10) |
| H(152) | 0·601 (2) | 0·015 (5) | 0·462 (2) | 0·091 (11) |
| H(153) | 0·655 (3) | 0·148 (4) | 0·445 (2) | 0·073 (9) |
| H(161) | 0·318 (3) | 0·232 (4) | 0·362 (2) | 0·098 (12) |
| H(162) | 0·419 (2) | 0·218 (4) | 0·330 (2) | 0·072 (9) |
| H(163) | 0·377 (2) | 0·081 (5) | 0·367 (2) | 0·083 (10) |
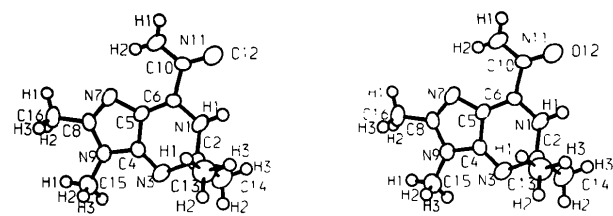


Fig. 1. Stereoscopic view showing atom-numbering system. (Ellipsoids correspond to 50% probability level.)
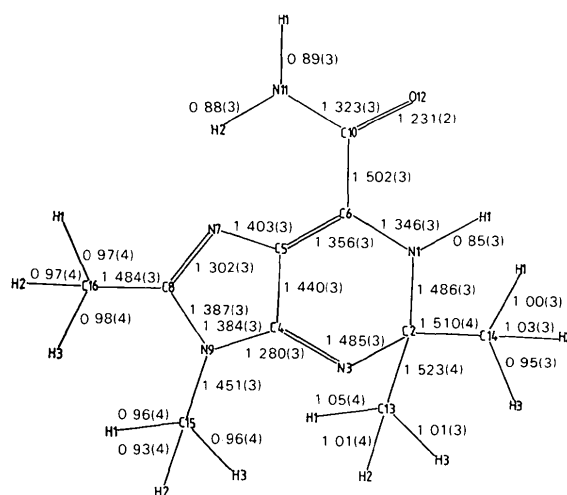


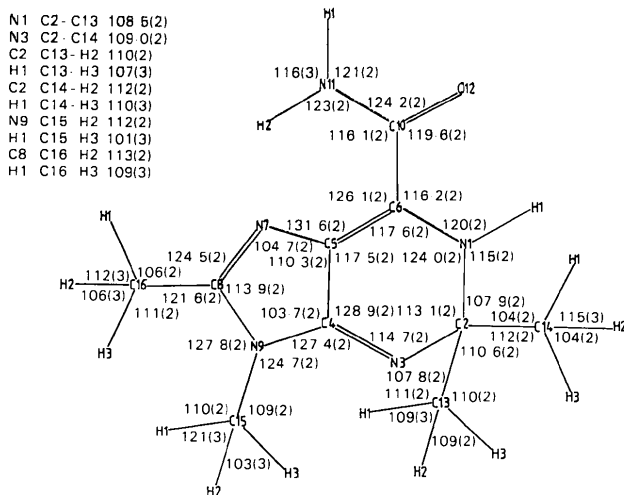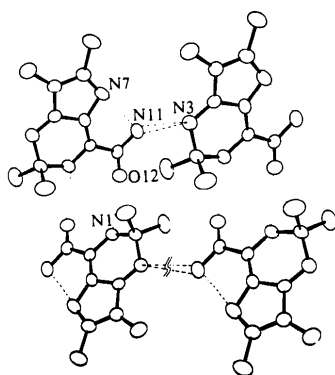Fig. 2. Bond lengths (Å), with e.s.d.'s in parentheses.

| | | | |
|---|---|---|---|
| N1 | C2- | C13 | 108 6(2) |
| N3 | C2- | C14 | 109 0(2) |
| C2 | C13- | H2 | 110(2) |
| H1 | C13- | H3 | 107(3) |
| C2 | C14- | H2 | 112(2) |
| H1 | C14- | H3 | 110(3) |
| N9 | C15 | H2 | 112(2) |
| H1 | C15 | H3 | 101(3) |
| C8 | C16 | H2 | 113(2) |
| H1 | C16 | H3 | 109(3) |



Fig. 3. Bond angles (°), with e.s.d.'s in parentheses.



Fig. 4. View indicating hydrogen bonding.

the final fractional coordinates and isotropic vibrational parameters. Fig. 1 is a stereoscopic view of the molecule (Johnson, 1965), and also shows the atom-numbering scheme. Figs. 2 and 3 give bond lengths and angles. Fig. 4 shows the hydrogen bonding.

**Discussion.** Best least-squares planes through ring atoms are given in Table 2. The five-membered ring is closely planar, and C(2) and N(3) of the six-membered ring deviate only by up to 0·1 Å from this plane. Contrastingly, ring atoms N(1) and C(6), and C(10), N(11) and O(12) of the carbamoyl group all lie on the same side of this plane, deviations 0·17–0·44 Å, probably because of the interpenetrating hydrogen-bonding network (see below). However, when the molecule is considered in terms of the best plane through eight of the nine ring atoms [omitting C(2) which is in tetrahedral coordination] the general conformation of the 1,2-dihydropurine ring system is revealed. The eight atoms are coplanar to within 0·1 Å,

whereas C(2) is 0·24 Å from their plane. The bond lengths and angles (Figs. 2 and 3) suggest that only C(2) is exluded from the conjugation of the ring system; inclusion of N(1) can be inferred by its almost planar triple coordination as well as by its situation in the general ring plane. N(9) and N(11) are similarly in planar coordination and engaged in conjugation. The full extent of the conjugated system embraces the amide group, whose atoms lie close to the plane of the rings. However, the degree of conjugation between amide group and ring system may be low, as indicated by the C(6)—C(10) bond length [1·502 (3) Å] which matches well with lengths of exocyclic bonds in a group of aromatic amides including p-nitrobenzamide [1·501 (2) Å] (Di Rienzo, Domenicano & Serantoni, 1977) rather than bonds in 5-amino-1-β-D-ribo-furanosylimidazole-4-carboxamide and its 5'-(di-hydrogen phosphate) [1·437 (6) and 1·455 (9) Å] (Adamiak & Saenger, 1979). In TDC, therefore, the coplanarity of amide and rings is more likely due to hydrogen bonding, including the internal N(11)···N(7) hydrogen bond, than conjugation, and the ring dimensions are likely to be little affected by the 6-carbamoyl substituent.

The break in conjugation at C(2) inevitably leads to bonding in the six-membered ring which is weakly delocalized compared with purines and isoguanine derivatives. Thus C(2)—N(1) and C(2)—N(3) are typical of C—N bonds in aliphatic amines, and the

Table 2. *Least-squares planes and distances of atoms from planes* (Å)

(a) Plane through atoms of five-membered ring

$$0.3996x' + 0.8200y' - 0.4097z' = 0.4086$$

(b) Plane through all ring atoms, except C(2)

$$0.4121x' + 0.7874y' - 0.4584z' = -0.0341$$

(x', y', z' are orthogonalized coordinates)

| | Plane (a) | Plane (b) |
|---|---|---|
| N(1) | 0·246 (3) | 0·057 (2)* |
| C(2) | −0·099 (3) | −0·241 (3) |
| N(3) | 0·021 (3) | −0·034 (2)* |
| C(4) | −0·003 (2)* | −0·034 (2)* |
| C(5) | 0·003 (2)* | −0·074 (2)* |
| C(6) | 0·177 (3) | 0·019 (2)* |
| N(7) | −0·002 (2)* | −0·029 (2)* |
| C(8) | 0·000 (2)* | 0·045 (2)* |
| N(9) | 0·002 (2)* | 0·050 (2)* |
| C(10) | 0·359 (3) | 0·142 (3) |
| N(11) | 0·416 (3) | 0·230 (3) |
| O(12) | 0·442 (3) | 0·153 (3) |
| C(13) | −1·543 (5) | −1·702 (5) |
| C(14) | 0·838 (5) | 0·667 (5) |
| C(15) | −0·046 (5) | 0·072 (5) |
| C(16) | −0·004 (5) | 0·115 (5) |

\* Atoms in least-squares fit.

other ring bond lengths contrast with the lengths observed in isoguanines (Banerjee, Saenger, Lesyng, Kazimierczuk & Shugar, 1978; Subramanian & Marsh, 1971) which have the same ring-bond pattern but different substituents; especially, $C(2)Me_2$ becomes $C(2)=O$ which permits complete delocalization round the ring. The delocalization in the six-membered ring of TDC is illustrated by comparison with dihydropyridine derivatives (Hisano et al. 1979), in which the bonds corresponding to $C(5)=C(6)$ and $C(4)-C(5)$ are, respectively, substantially shorter and slightly longer than in TDC, demonstrating the opportunity for conjugation in TDC embracing $N(1)$ and the five-membered ring.

A search of the Cambridge Crystallographic Data Base accessed via the Crystal Structure Search Retrieval (1980) system (CSSR) revealed no other 1,2-dihydropurine structures. The only closely related structures found were the isoguanines referred to above, but one other structure (I) (Tinant, Germain, Declercq & Van Meerssche, 1980) substituted with double bonds at $C(4)$ and $C(5)$ of the five-membered ring was retrieved.

Although molecule (I) has $C=O$ in place of the $C(4)=N(3)$ bond of TDC, the dimensions of the five-membered rings in the two molecules are similar; of particular note are the $C-N$ bonds ($a, b, c$ in I) which are approximately equal in length, $1\cdot38-1\cdot41$ Å in both molecules.
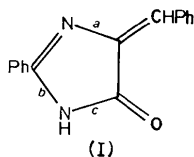


(I)

Table 3. *Geometry of hydrogen bonds*

| $A-H\cdots B$ | $A\cdots B$ | $A-H$ | $H-B$ | $\angle A-H\cdots B$ |
|---|---|---|---|---|
| $N(1)-H(11)\cdots O(12^i)$ | $3\cdot106$ (3) Å | $0\cdot85$ (3) Å | $2\cdot28$ (3) Å | $165$ (2)° |
| $N(11)-H(111)\cdots N(3^{ii})$ | $3\cdot156$ (3) | $0\cdot89$ (3) | $2\cdot27$ (3) | $177$ (2) |
| $N(11)-H(112)\cdots N(7)$ | $2\cdot885$ (3) | $0\cdot88$ (3) | $2\cdot20$ (3) | $135$ (2) |

Symmetry operations: (i) $1 - x, y, 1\frac{1}{2} - z$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$.

The molecules form an interpenetrating hydrogen-bonding network (Fig. 4, Table 3). All the hydrogen bonds involve the carbamoyl group, including the intramolecular bond $[N(11)\cdots N(7) = 2\cdot89$ Å]. The network is built up of hydrogen-bonded dimers in which the two component TDC molecules are related by the twofold axis with $N(1)\cdots O(12^i) = 3\cdot11$ Å. The dimers are linked to each other through $N(11)\cdots N(3^{ii}) = 3\cdot16$ Å.

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