organic compounds

A hydrogen-bonded 'trimer' of two symmetric dipyridones[1]

Emily F. Maverick,[a]* Paul L. Wash[b]‡ and David A. Lightner[b]

[a]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA, and [b]Department of Chemistry, University of Nevada, Reno, NV 89557-0020, USA

Correspondence e-mail: maverick@chem.ucla.edu

The isomers 3,3′-(1,2-ethynediyl)bis(2-pyridone), (I), and 6,6′-(1,2-ethynediyl)bis(2-pyridone), (II), were designed to form a hydrogen-bonded pair through alignment of their complementary cyclic lactam moieties. Instead, an equimolar mixture of (I) and (II) dissolved in methanol produced crystals of 3,3′-(1,2-ethynediyl)bis(2-pyridone)–6,6′-(1,2-ethynediyl)bis(2-pyridone)–methanol (1/2/2), $0.5C_{12}H_8N_2O_2 \cdot C_{12}H_8N_2O_2 \cdot CH_4O$, in which one molecule of (I), situated at a center of symmetry, is hydrogen bonded to two molecules of (II) and to two molecules of methanol.

Comment

The symmetric dipyridone (I) was synthesized as part of an ongoing study of substituted pyridones. The dimerization of 2-pyridones through hydrogen bonding has often been
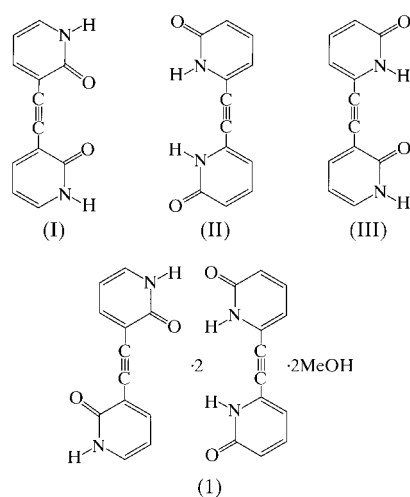
observed (for example, see Maverick *et al.*, 1993). In principle, (I) and (II), being complementary in their structures, could

associate to form a 'dimer' which might be more soluble in relatively non-polar solvents than random hydrogen-bonded oligomers. The behavior of symmetric dipyridone (II) and asymmetric dipyridone (III) in solution and in the solid state had been investigated by Ducharme & Wuest (1988). They observed that (III) self-associates in solution and in the crystal, as does a similarly asymmetric compound with one pyridone and one carboxylic acid function (Wash *et al.*, 1997). On the other hand, (II) is only about 20% associated in solution, and in the crystal is polymeric.

We found (I) and (II) to be insoluble in non-polar solvents. Solutions equimolar in (I) and (II) in dimethyl sulfoxide or methanol show no evidence for association. This is not unexpected as both solvents participate (and compete) in hydrogen bonding. We report here that association does take place in the solid state, but it is mediated by methanol, the solvent from which crystals of the title compound, (1), were grown. In addition, though (II) is found in the conformation shown in the scheme, (I) is centrosymmetric, with each of its pyridone groups hydrogen bonded to one of the pyridones of (II) and to one molecule of methanol. The second lactam nitrogen (N10) of each molecule of (II) is hydrogen bonded to the methanol, connecting (II) with (I) in an N—H⋯O—H⋯O=C arrangement, while the lactam O16 atom par-
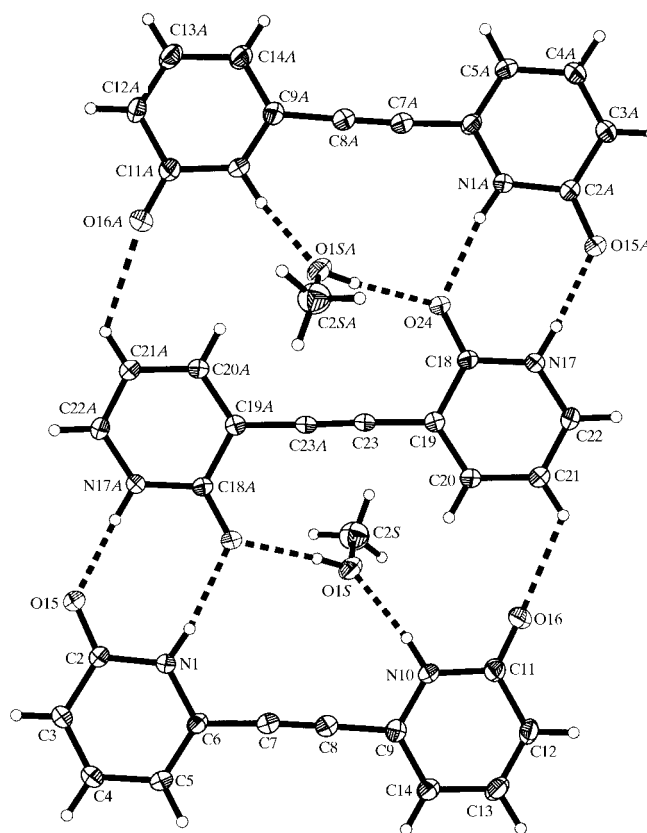

Figure 1
A view of the unit-cell contents showing the hydrogen-bonded arrangement of one molecule of (I), center, with two molecules of (II), top and bottom, and with two molecules of methanol solvent. The A atoms are related to the numbered atoms by the center of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Dashed lines indicate hydrogen bonds. The C21—H21⋯O16 'weak hydrogen bond' is also shown. Ellipsoids enclose 50% probability.

ticipates in two short C=O···H—C contacts (Fig. 1 and Table 1).

The planes of the centrosymmetrically related six-membered rings in (I) are parallel, but the normals to the two unique ring planes in (II) form an angle of 9.89 (12)°. Thus, (II) in the present structure is more nearly planar than (III) in the dimeric complex (interplanar angle 29°; Ducharme & Wuest, 1988).

The hydrogen bonding between the cyclic lactam moieties may be compared to that found in 13 related fragments (Maverick *et al.*, 1993), in which N···O distances across the lactam–lactam motif average 2.82 (5) Å. The corresponding N···O distances (Fig. 1 and Table 1) in the present structure are consistent with the average, even though the methanol is also involved in the intermolecular interaction. The angle between the normals to the planes of the two six-membered rings (N1—C6 and N17A—C22A) is 9.16 (13)°, and the N—H···O bonding angles are nearly linear. Though two of the pyridone rings in the 'trimer' are not involved in lactam–lactam hydrogen bonding, the complex may be quite stable. Recently, the strength of a C—H···O 'weak hydrogen bond' has been estimated to be as much as half that of an N—H···O=C hydrogen bond (Vargas *et al.*, 2000).

The conformation of (I) with mirror symmetry shown in the scheme was approximated by rotation of one pyridone ring of centrosymmetric (I) by 180° using the program *OPEC* (Gavezzotti, 1983). The two O atoms in the planar mirror-symmetric conformation would be about 4.31 Å apart, too close to allow the observed solvation by methanol. This suggests that the observed conformation of (I) predominates in methanol solution. Neither the expected 'dimer' of (I) and (II), nor a 'trimer' with the opposite composition, two molecules of mirror-symmetric (I) joined to one molecule of centrosymmetric (II), would be likely to form.

Experimental

Dipyridone (II) was prepared according to the method outlined in Ducharme & Wuest (1988), whereas the synthesis of (I) required more steps. In a strategy similar to the synthesis of asymmetric dipyridone (III) described in the same paper, dipyridone (I) was prepared by brominating commercially available 2-pyridone to give 3-bromo-2-pyridone, protecting the keto group by benzylation to give 2-(benzyloxy)-3-bromopyridine, and coupling the latter with (trimethylsilyl)acetylene under conditions described by Takahashi *et al.* (1980). Desilylation and coupling of the resulting alkyne with 2-(benzyloxy)-3-bromopyridine and debenzylation with trifluoroacetic acid gave (I). Crystals were prepared by vapor diffusion of diethyl ether into an equimolar solution of (I) and (II) in methanol.

Crystal data

$0.5C_{12}H_8N_2O_2 \cdot C_{12}H_8N_2O_2 \cdot CH_4O$
$M_r = 350.35$
Triclinic, $P\bar{1}$
$a = 7.334\ (4)$ Å
$b = 10.791\ (6)$ Å
$c = 11.543\ (7)$ Å
$\alpha = 69.70\ (2)°$
$\beta = 75.01\ (2)°$
$\gamma = 86.653\ (15)°$
$V = 827.2\ (8)$ Å^3

$Z = 2$
$D_x = 1.407$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.9$–$10.3°$
$\mu = 0.101$ mm^{-1}
$T = 156$ K
Parallelepiped, colorless
$0.50 \times 0.30 \times 0.30$ mm

Data collection

Picker (Crystal Logic) diffractometer
Profile data from $\theta/2\theta$ scans
4819 measured reflections
4819 independent reflections
2561 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30°$

$h = -10 \rightarrow 0$
$k = -15 \rightarrow 14$
$l = -16 \rightarrow 15$
3 standard reflections
  every 97 reflections
  intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.176$
$S = 1.079$
4816 reflections
237 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0540P)^2 + 0.4326P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O24^i	0.86	2.01	2.864 (3)	170
N17—H17···O15^i	0.86	1.86	2.715 (3)	171
N10—H10···O1S	0.86	1.93	2.776 (3)	168
O1S—H1S···O24^i	0.82	1.90	2.712 (3)	172
C21—H21···O16	0.93	2.52	3.152 (3)	126
C22—H22···O16^{ii}	0.93	2.46	3.379 (3)	170

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

The structure was solved in the space group $P1$. The center of symmetry was readily located, and refinement continued in $P\bar{1}$. Three reflections (210, 200, and $\bar{2}11$) were omitted from the refinement because their intensities were too strong to be measured precisely. H atoms were constrained geometrically with bond distances C—H 0.93–0.96, N—H 0.86, and O—H 0.82 Å, and U_{iso} equal to $1.2U_{eq}$ of the attached atom. For methanol, the torsion angles determining the conformations of the methyl and hydroxyl groups were refined.

Data collection: *COLLECT* (UCLA, 1984); cell refinement: *LEAST* (UCLA, 1984); data reduction: *REDUCE* (UCLA, 1984); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1995).

References

Ducharme, Y. & Wuest, J. D. (1988). *J. Org. Chem.* **53**, 5787–5789.
Gavezzotti, A. (1983). *J. Am. Chem. Soc.* **105**, 5220–5225.
Maverick, E., Chiefari, J. & Lightner, D. A. (1993). *Acta Cryst.* C**49**, 338–340.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Sheldrick, G. M. (1995). *SHELXTL.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin.
Takahashi, S., Kuroyama, Y., Sonogashira, K. & Hagihara, N. (1980). *Synthesis*, pp. 627–630.
UCLA (1984). *UCLA Crystallographic Package.* J. D. McCullough Laboratory of X-ray Crystallography, University of California, Los Angeles, USA.
Vargas, R., Garza, J., Dixon, D. A. & Hay, B. P. (2000). *J. Am. Chem. Soc.* **122**, 4750–4755.
Wash, P. L., Maverick, E., Chiefari, J. & Lightner, D. A. (1997). *J. Am. Chem. Soc.* **119**, 3802–3806.