0·057, −0·058, −0·026, 0·027 Å from the best least-squares tetraaza plane are observed for N(1), N(2), N(3) and N(5), with the pyridine ring making an angle of 21·7° to this plane. Both amide H atoms are directed inside the macrocycle and are hydrogen bonded to the adjacent amine N atoms. The hexahydropyrimidine ring is in a chair conformation with equatorial N(1)—C(5) and N(2)—C(17) bonds. It is roughly perpendicular to the monocyclic plane defined above, as shown by the angle of 79·9° between the N(1), N(2), N(3), N(5) and C(1), C(2), C(3), C(4), N(1), N(2) least-squares planes. The lone pairs of the N(1) and N(2) atoms point inside the cavity of the macroring. The whole structure adopts a pseudo-C_s symmetry with a pseudo-mirror plane passing through atoms N(4), C(10), C(1) and C(4). This configuration is rather rigid and is maintained in solution as evidenced by ^{1}H and ^{13}C NMR spectroscopy. We can conclude that the existence of a well defined cavity is largely due to the rigidification introduced by the C(1) bridge between N(1) and N(2) compared to the more flexible compound (2), and to hydrogen bonding between amide protons and amine N atoms. Compound (1) is well designed for complexation studies of metal ions inside the cavity.

We are indebted to Dr Anne Renault for helpful discussions and skillful assistance.

References

Dutasta, J. P., Gellon, G., Leuchter, C. & Pierre, J. L. (1988). *J. Org. Chem.* **53**, 1817–1819.

Enraf–Nonius (1977). *Structure Determination Package,* version RSX11M. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Table 2.2*B*. Birmingham: Kynoch Press. (Present distributor: Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lehn, J. M. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 89–112.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Melson, G. A. (1979). *Coordination Chemistry of Macrocyclic Compounds.* New York: Plenum.

Acta Cryst. (1990). **C46**, 261–263

Structure of a 1,2,3,5-Tetrazin-4-one

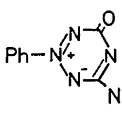
By Kentaro Yamaguchi, Akio Ohsawa, Takashi Itoh and Chikako Kawabata

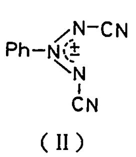
School of Pharmaceutical Sciences, Showa University, 1-5-8 *Hatanodai, Shinagawa-ku, Tokyo* 142, *Japan*

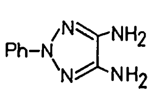
(*Received* 5 *April* 1989; *accepted* 17 *May* 1989)

Abstract. 6-Amino-2-phenyl-1,2,3,5-tetrazin-4-one, $C_8H_7N_5O$, $M_r = 189{\cdot}2$, monoclinic, $P2_1/n$, $a = 12{\cdot}880\,(1)$, $b = 9{\cdot}427\,(1)$, $c = 7{\cdot}166\,(1)$ Å, $\beta = 100{\cdot}95\,(1)°$, $V = 854{\cdot}2\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}471$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}54050$ Å, $\mu = 0{\cdot}899$ mm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0{\cdot}054$ for 1206 observed reflexions. The six-membered tetrazine ring is planar indicating extensive electron delocalization. There are two intermolecular hydrogen bonds: N(8)···N(5) 3·041 (4) and N(8)···O(7) 2·883 (4) Å.

Introduction. 1,2,3,5-Tetrazines, of which few derivatives have been reported (Baydar, Boyd, Lindley & Walton, 1985; Butler, Cunningham, McArdle & O'Halloran, 1988), are the rarest studied class of the three possible tetrazine ring systems (Neunhoeffer, 1984). Recently, we obtained a 1,2,3,5-tetrazine (6-amino-2-phenyl-1,2,3,5-tetrazin-4-one) (I) from photoreaction of (*E*,*Z*)-1,3-dicyano-2-phenyltriazene (II). The present paper describes details of the structure analysis of this novel heterocyclic compound having a 1,3-dipolar azimine moiety.


(I)


(II)


(III)

Experimental. Compound (II) was prepared by oxidation of 4,5-diamino-2-phenyl-1,2,3-triazole (III) (Thiele & Schleussner, 1897) using Pb(OAc)$_4$ in CH_2Cl_2. A solution of (II) in CH_3OH (hygroscopic) was irradiated by a medium-pressure mercury lamp for 7·5 min to give the compound (I). Recrystallization from C_2H_5OH gave colourless prisms having m.p. 530–532 K. The combustion analysis was consistent with the structure for this compound.

0108-2701/90/020261-03$03.00

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
N(1)	0·9190 (1)	0·3362 (2)	0·1320 (3)	2·85 (7)
N(2)	0·9990 (1)	0·4115 (2)	0·2182 (3)	2·47 (6)
N(3)	1·0963 (2)	0·3752 (2)	0·2717 (4)	3·07 (7)
C(4)	1·1192 (2)	0·2324 (3)	0·2340 (4)	2·95 (9)
N(5)	1·0425 (1)	0·1451 (2)	0·1451 (3)	2·84 (7)
C(6)	0·9470 (2)	0·1992 (3)	0·0944 (4)	2·52 (8)
O(7)	1·2110 (1)	0·1945 (2)	0·2855 (4)	4·55 (8)
N(8)	0·8676 (2)	0·1215 (3)	0·0027 (4)	3·23 (8)
C(9)	0·9733 (2)	0·5591 (3)	0·2577 (4)	2·84 (8)
C(10)	0·8692 (3)	0·6023 (3)	0·2138 (5)	3·85 (10)
C(11)	0·8463 (3)	0·7427 (4)	0·2524 (6)	4·71 (12)
C(12)	0·9266 (4)	0·8335 (4)	0·3317 (6)	4·78 (13)
C(13)	1·0289 (3)	0·7877 (4)	0·3725 (5)	4·47 (12)
C(14)	1·0545 (3)	0·6485 (3)	0·3368 (5)	3·61 (10)

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)—N(2)	1·306 (3)	N(2)—C(9)	1·470 (4)
N(2)—N(3)	1·285 (4)	C(9)—C(10)	1·380 (5)
N(3)—C(4)	1·416 (4)	C(10)—C(11)	1·395 (6)
C(4)—N(5)	1·349 (4)	C(11)—C(12)	1·379 (6)
N(5)—C(6)	1·317 (4)	C(12)—C(13)	1·365 (7)
C(6)—N(1)	1·382 (4)	C(13)—C(14)	1·389 (5)
C(4)—O(7)	1·223 (4)	C(14)—C(9)	1·379 (5)
C(6)—N(8)	1·326 (4)		
N(1)—N(2)—N(3)	129·3 (2)	N(5)—C(6)—N(8)	120·9 (2)
N(2)—N(3)—C(4)	114·9 (2)	N(1)—C(6)—N(8)	114·0 (2)
N(3)—C(4)—N(5)	120·7 (2)	C(9)—C(10)—C(11)	117·9 (3)
C(4)—N(5)—C(6)	117·0 (2)	C(10)—C(11)—C(12)	120·0 (4)
N(5)—C(6)—N(1)	125·0 (2)	C(11)—C(12)—C(13)	120·6 (3)
C(6)—N(1)—N(2)	112·8 (2)	C(12)—C(13)—C(14)	120·8 (3)
N(1)—N(2)—C(9)	114·7 (2)	C(13)—C(14)—C(9)	117·7 (3)
N(3)—N(2)—C(9)	115·8 (2)	C(14)—C(9)—C(10)	122·7 (3)
N(3)—C(4)—O(7)	116·3 (2)	N(2)—C(9)—C(10)	118·7 (3)
N(5)—C(4)—O(7)	122·9 (3)	N(2)—C(9)—C(14)	118·5 (3)

Intensity data collected from a crystal of dimensions 0·30 × 0·15 × 0·50 mm. D_m not measured. Rigaku AFC5 four-circle diffractometer used with θ–2θ scan method, scan width $(1{\cdot}3 + 0{\cdot}41\ \tan\theta)^\circ$ and scan speed 16° min^{-1}. Lattice parameters obtained from least-squares analysis of 20 reflexions with 2θ values ranging from 56 to 61°. Out of 1517 reflexions scanned within index range h: $-14\rightarrow14$, k:$0\rightarrow10$, l:$0\rightarrow8$ up to $(\sin\theta)/\lambda \le 0{\cdot}56$ Å^{-1} including 120 equivalent reflexions ($R_{\rm int} = 0{\cdot}018$), 1271 unique reflexions classified as observed. Three standard reflexions measured every 120 reflexions. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied. Structure solved using program package *SAPI85* (Yao, Zheng, Qian, Han, Gu & Fan, 1985) version of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-H atoms. Function minimized $\sum w[|(|F_o|)^2-(|F_c|)^2|]^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}02(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics. All H atoms were located from the difference map. Their initial thermal parameters were set at the equivalent isotropic thermal parameter of the bonded atoms. Final discrepancy indices $R = 0{\cdot}054$, $wR = 0{\cdot}073$, $S = 2{\cdot}590$ for 1206 reflexions with $F > \sigma(F)$. Max. $\Delta/\sigma < 0{\cdot}08$ in the final least-squares cycle. Final difference Fourier map showed no residuals greater than 0·38 e Å^{-3}. All calculations performed using a PANAFACOM computer with *RCRYSTAN* (Rigaku Corporation, Tokyo, Japan) X-ray analysis program system. The atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for this molecule are listed in Table 1.* The bond lengths and

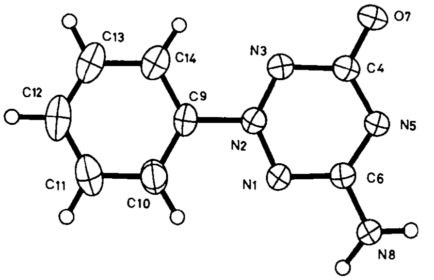


Fig. 1. *ORTEP* drawing (Johnson, 1965). Thermal ellipsoids are drawn at the 50% probability level while hydrogen isotropic thermal parameters are represented by spheres of arbitrary size.

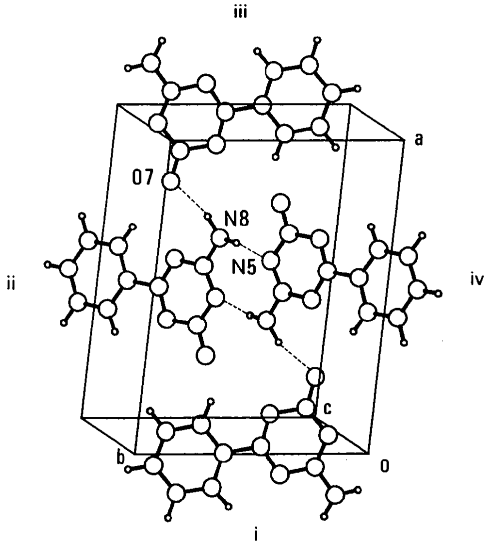


Fig. 2. The crystal structure. Symmetry operations for the molecule are: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+2, y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

---

* Lists of structure amplitudes, anisotropic thermal parameters, least-squares planes with deviations and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52244 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles are listed in Table 2. Fig. 1 shows the *ORTEP* drawing (Johnson, 1965) of the molecule with atomic labeling. Fig. 2 presents the crystal structure.

The tetrazinone ring is almost planar, with maximum displacement out of the least-squares plane of $-0·010$ (5) Å for N(1) and N(3). This planarity and the endocyclic bond distances indicate an extensive delocalization of electron density which also extends over N(8) and O(7). The N(2)—N(3), N(5)—C(6) and C(4)—O(7) distances, 1·285 (4), 1·317 (4) and 1·223 (4) Å, respectively, indicate the contribution of canonical form (I) shown in the *Introduction*. The N(2)—N(1)—C(6) angle of 112·8 (2)° inclinable to sp^3 hybridization also indicates the localization of an electron (negative charge) on the N(1) position. However, the delocalizability of the electron density in this ring is higher than that found in 4-dimethylamino-1-phenyl-1,2,3,5-tetrazin-6-one (Lindley, Walton, Baydar & Boyd, 1985) because of its poor planarity [maximum displacement out of the least-squares plane of $-0·070$ (6) Å] and contribution of the canonical form [1·278 (4), 1·312 (6), 1·213 (6) Å, respectively, for corresponding double-bond lengths in the tetrazinone ring].

Though the C(9)—N(2) distance of 1·470 (4) Å indicates a single-bond linkage between sp^2-hybridized C and N atoms, the dihedral angle between the heterocyclic and phenyl-ring planes is small [4·2 (2)°]. This indicates the attractive interactions at H(10)···N(1) and H(14)···N(3) [H(10) and H(14) are connected to C(10) and C(14), respectively], whose short contacts are 2·34 (2) and 2·35 (3) Å, respectively (Taylor & Kennard, 1982).

In the crystal structure of this compound the hydrogen bonds N(8)···N(5) [3·041 (4) Å] and N(8)···O(7) [2·883 (4) Å] are observed.

References

Baydar, A. E., Boyd, G. V., Lindley, P. F. & Walton, A. R. (1985). *J. Chem. Soc. Parkin Trans.* 1, pp. 415–418.

Butler, R. N., Cunningham, D., McArdle, P. & O'Halloran, G. A. (1988). *J. Chem. Soc. Chem. Commun.* pp. 232–234.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Lindley, P. F., Walton, A. R., Baydar, A. E. & Boyd, G. V. (1985). *Acta Cryst.* **C41**, 1669–1672.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Neunhoeffer, H. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 3, edited by A. J. Boulton & A. McKillop, pp. 531–572. Oxford: Pergamon Press.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Thiele, J. & Schleussner, K. (1897). *Justus Liebigs Ann. Chem.* **295**, 129.

Yao, J.-X., Zheng, C.-D., Qian, J.-Z., Han, F.-S., Gu, Y.-X. & Fan, H.-F. (1985). *SAPI85. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Institute of Physics, Academia Sinica, Beijing, People's Republic of China.

Acta Cryst. (1990). C46, 263–267

Structure of Tetramethyl (2*R*,3*R*,11*R*,12*R*)-*α*-Benzyl-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetra[(2*S*)-carboxamidoacetate] (an 18-Crown-6 Derivative)

By P. Singh, M. L. Miles and S. Davis

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, *USA*

(*Received* 12 *December* 1988; *accepted* 9 *May* 1989)

Abstract. $C_{56}H_{68}N_4O_{18}$, $M_r = 1085·18$, monoclinic, $P2_1$, $a = 9·750$ (3), $b = 21·389$ (6), $c = 13·999$ (5) Å, $\beta = 93·22$ (3)°, $V = 2915$ (2) Å^3, $Z = 2$, $D_x = 1·24$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71096 Å, $\mu = 0·9$ cm^{-1}, $F(000) = 1152$, $T = 295$ K, $R = 0·050$ for 3903 unique reflections. The 18-crown-6 moiety of the molecule has approximate C_2 symmetry, the pseudo twofold axis passing through the midpoints of the C—C bonds containing the side chains. The six O—C—C—O segments have the conformations g^+g^-a, ag^+a, ag^-a, ag^+a, ag^-g^+ and ag^-a. The two *gga* conformations have caused unusual bending in the crown ring resulting in intramolecular inter side-chain hydrogen bonding. One of these hydrogen bonds covers the top face of the crown and the other covers the bottom face. Molecules along the *a* axis form a polymeric chain *via* a pair of N—H···O hydrogen bonds.

Introduction. Macrocyclic polyethers, also known as 'crown' ethers owing to the appearance of their molecular models, have the remarkable property of

0108-2701/90/020263-05$03.00