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The Crystal and Molecular Structure of 3-(*N*-Benzil)aminopyrrolidine-2,5-dione Monohydrate

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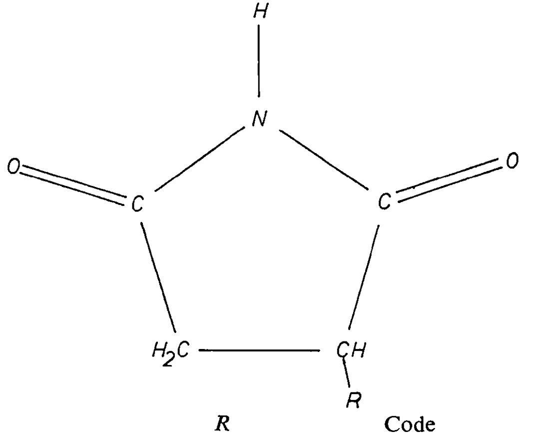
3-(*N*-Benzil)aminopyrrolidine-2,5-dione monohydrate crystallizes in the orthorhombic space group *Pbca* with $a=23{\cdot}943$ (10), $b=9{\cdot}526$ (10), $c=9{\cdot}834$ (10) Å, $Z=8$. The structure was solved by direct methods and refined by least-squares methods to an R of 0·071 with 1754 diffractometric intensities. All but four hydrogen atoms were located from a difference map. The bond lengths and angles in the five-membered ring agree well with the corresponding values in other succinimide derivatives. Each water molecule is surrounded by four organic molecules and forms one weak and three strong hydrogen bonds. The water molecules (with identical x and rather similar y coordinates) are located nearly above each other at a distance of $z=\frac{1}{2}$. This column of water molecules has a pseudo-4_1 axis with respect to their hydrogen atoms and to each of the four hydrogen bonds.

Introduction

3-(*N*-Benzil)aminopyrrolidine-2,5-dione monohydrate (hereafter BA-PD) belongs to the group of monosubstituted succinimide derivatives, (*a*), (*b*), (*c*), which were synthesized and studied systematically for pharmaceutical purposes by Seres (1970) at the Chinoin Factory. The crystal structures of (*a*) and (*b*) have been described (Argay & Kálmán, 1973; Argay & Carstensen-Oeser, 1973). The structure of BA-PD (*c*) is of particular interest owing to an additional water molecule, the presence of which has been revealed in the course of X-ray study.



	R	Code
(*a*)	C_6H_5–	PH-PD
(*b*)	C_6H_5–NH–	PHA-PD
(*c*)	C_6H_5–CH_2–NH–	BA-PD

Experimental

The bulky crystals were obtained from a mixture of water and ethanol. Lattice parameters were found from Weissenberg photographs and refined on a diffractometer.

Crystal data

$C_{11}H_{12}N_2O_2.H_2O$, M.W. 222·24, orthorhombic,
$a=23{\cdot}973$ (10), $b=9{\cdot}526$ (10), $c=9{\cdot}834$ (10) Å,
$V=2245{\cdot}7$ Å^3, $Z=8$,
$D_c=1{\cdot}315$, $D_x=1{\cdot}323$ g cm^{-3} (by flotation),
$F(000)=944$,
μ for Cu $K\bar{\alpha}$ ($\lambda=1{\cdot}5418$ Å$)=8{\cdot}1$ cm^{-1}.
Space group *Pbca* (No. 61).

The intensities were measured on a Stoe–Güttinger automatic Weissenberg goniometer in equi-inclination arrangement. 346 of the total 1754 independent reflexions with $I-2{\cdot}0\sigma(I)\geq 0$ were taken as unobserved. After data reduction an absolute scale factor and overall isotropic temperature factor $B=4{\cdot}25$ Å^2 were determined by Wilson's method.

Structure determination and refinement

The phase problem for 212 reflexions with $E>1{\cdot}40$ was solved by the program *MULTAN* (Germain, Main & Woolfson, 1971). The E map computed from the best set with an *ABSFOM* of 1·639 gave the position of all 15 non-hydrogen atoms, including the oxygen of an additional water molecule. A structure-factor calculation, based on the fractional coordinates obtained from the E map with an overall isotropic temperature factor of $B=4{\cdot}25$ Å^2, resulted in an R of 0·337 for the observed reflexions.

The structure was refined by least-squares calculations, minimizing the function $\sum w(|F_o|-1/G|F_c|)^2$ with the weighting scheme

$$w=(8+F_o+0{\cdot}2F_o^2)^{-1}$$

suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). Three cycles of isotropic and three of anisotropic refinement reduced R to 0·116. At this

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stage the positions of 10 out of 14 hydrogen atoms were located from a difference map. Two further cycles of anisotropic refinement of the non-hydrogen parameters with fixed hydrogen positions reduced *R* to 0·091.

Location of the remaining four hydrogen atoms was carried out geometrically. The O(*W*) atom of the water molecule is surrounded by four BA-PD molecules at

i x, y, z; ii $-x, -y, 1-z$;
iii $-x, \frac{1}{2}+y, \frac{1}{2}-z$; iv $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The four shortest intermolecular distances directed to O(*W*):

O(*W*)···N(2^{iii}) 2·81 Å
O(*W*)···N(1^{i}) 2·88
O(*W*)···O(1^{iv}) 2·91
O(*W*)···N(2^{ii}) 3·26

form a distorted tetrahedron. The plane *P*(1)* of this tetrahedron determined by N(1), O(*W*) and N(2^{iii}) is almost perpendicular (97·3°) to the plane *P*(2) formed by O(1), O(*W*) and N(2^{ii}). On the assumptions that H(N2) lies approximately in the plane of the succinimide ring and O(1) can be only an acceptor, the hydrogen atoms of the water molecule must be near to the plane *P*(2) with the hydrogen atoms belonging to N(1) and N(2^{iii}) directed towards O(*W*). These conditions determined the very probable positions of the missing four hydrogens. Two further cycles of anisotropic refinement of the heavy-atom parameters with the hydrogen atoms treated isotropically resulted in a final *R* of 0·071 for the 1407 intensities observed (0·094 for all reflexions). It is noteworthy that the refinement accomplished after the introduction of the missing hydrogen atoms improved the average e.s.d.'s for bond lengths from 0·008 to 0·005 Å, and for angles from 0·6 to 0·4°.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Calculations to solve the phase problem (including data reduction, *etc.*) were performed on a TR-440 computer at the Computer Centre in Darmstadt, while structure refinement was carried out on an ICL-1903A computer in Budapest with the modified least-squares program of Albano, Domenicano & Vaciago (1966). The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1. The parameters of the hydrogen atoms and the X(C,N,O)–H distances are shown in Table 2. The structure factors are listed in Table 3. The interatomic distances and bond angles are given in Table 4.

Table 2. *Fractional coordinates* (×10³) *isotropic temperature parameters* (Å²) *and bond distances* (Å) *for the hydrogen atoms*

Estimated standard deviations are given in parentheses.

	x	*y*	*z*	B_i	X–H
H(1)	87 (2)	347 (6)	458 (6)	1·6 (1·2)	0·99
H(2)	139 (2)	546 (6)	420 (6)	3·4 (1·4)	0·97
H(3)	230 (3)	577 (8)	537 (7)	6·7 (1·8)	0·99
H(4)	268 (3)	396 (8)	653 (8)	8·7 (2·0)	1·01
H(5)	211 (2)	194 (5)	702 (5)	2·0 (1·0)	0·96
H(7)	122 (2)	117 (4)	355 (4)	1·0 (0·9)	1·03
H(91)	132 (2)	−164 (6)	470 (6)	3·5 (1·3)	1·04
H(92)	176 (2)	−83 (5)	381 (5)	2·7 (1·1)	0·97
H(111)	89 (2)	140 (6)	711 (6)	5·6 (1·4)	1·06
H(112)	139 (2)	41 (5)	643 (5)	2·5 (1·0)	0·99
H(*W*1)	−4 (2)	334 (7)	570 (7)	6·4 (1·7)	0·87
H(*W*2)	−39 (4)	248 (11)	565 (10)	17·5 (2·7)	0·68
H(N1)	36 (4)	142 (10)	523 (10)	17·9 (2·6)	1·10
H(N2)	54 (2)	−158 (7)	138 (6)	4·6 (1·5)	0·97

Table 1. *Fractional coordinates and anisotropic thermal parameters* (×10⁴) *for non-hydrogen atoms*

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form:

$$\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right].$$

	x	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	1243 (2)	3521 (5)	5014 (4)	20 (1)	102 (5)	79 (4)	−2 (3)	−5 (3)	−11 (7)
C(2)	1556 (2)	4716 (5)	4742 (5)	27 (1)	105 (5)	97 (5)	−19 (4)	19 (4)	−30 (8)
C(3)	2070 (2)	4911 (5)	5342 (6)	24 (1)	141 (6)	149 (6)	−36 (4)	24 (4)	−68 (10)
C(4)	2276 (2)	3917 (6)	6230 (6)	16 (1)	194 (8)	176 (7)	−19 (4)	7 (4)	−90 (12)
C(5)	1966 (2)	2693 (5)	6488 (5)	14 (1)	148 (6)	122 (5)	21 (3)	−15 (3)	−31 (9)
C(6)	1448 (2)	2499 (4)	5882 (4)	16 (1)	98 (4)	63 (3)	10 (3)	7 (3)	−35 (7)
C(7)	988 (2)	329 (4)	3889 (4)	16 (1)	90 (4)	58 (3)	−10 (3)	9 (3)	−7 (7)
C(8)	546 (2)	13 (4)	2816 (4)	17 (1)	91 (5)	57 (3)	6 (3)	1 (3)	12 (6)
C(9)	1363 (2)	−980 (4)	3861 (4)	15 (1)	108 (5)	72 (4)	10 (3)	−4 (3)	−10 (7)
C(10)	1171 (2)	−1793 (4)	2631 (4)	17 (1)	88 (5)	67 (4)	3 (3)	7 (3)	4 (7)
C(11)	1122 (2)	1173 (4)	6229 (4)	23 (1)	89 (5)	75 (4)	−7 (3)	−10 (3)	2 (7)
N(1)	724 (1)	727 (4)	5168 (3)	16 (1)	99 (4)	54 (3)	−1 (2)	3 (2)	−16 (6)
N(2)	699 (1)	−1151 (4)	2113 (3)	19 (1)	92 (4)	58 (3)	−1 (2)	−4 (2)	−13 (5)
O(1)	125 (1)	698 (3)	2605 (3)	21 (1)	156 (4)	78 (3)	41 (2)	−5 (2)	8 (6)
O(2)	1382 (2)	−2832 (3)	2165 (3)	32 (1)	122 (4)	100 (3)	44 (3)	−7 (3)	−39 (6)
O(*W*)	−190 (1)	2689 (3)	5200 (3)	17 (1)	147 (4)	74 (3)	−4 (2)	−12 (2)	11 (6)

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* Equation for plane *P*(1): $0{\cdot}6478X+0{\cdot}7615Y-0{\cdot}0246Z=1{\cdot}5319$, and for plane *P*(2): $-0{\cdot}8359X+0{\cdot}5422Y-0{\cdot}0859Z=1{\cdot}3312$.

Table 3. *Observed and calculated structure factors* (×10)

Discussion

The geometry of the succinimide ring is similar to that found in PH-PD (Argay & Kálmán, 1973) and in PHA-PD (Argay & Carstensen-Oeser, 1973). Mean values of the corresponding bond lengths and angles are given in Fig. 1 and are comparable with those given by Mason (1961) for succinimide. In tri-substituted succinimide derivatives, *e.g.* 'Morpholep' (Argay & Seres, 1973) and α-*p*-chlorophenyl-α-methyl-α′-cyanosuccinimide (Baudour & Messager, 1971), the bonding of the five-membered ring is also very similar to that shown in Fig. 1. The C–N bond lengths in the succinimide ring are identical within experimental error. Their double-bond orders *p*, expressed by the modified Coulson formula (Liquori & Vaciago, 1956), are 0·36 and 0·45 ($S = 1{\cdot}472$ Å, $D = 1{\cdot}270$ Å). The best plane of the succinimide ring forms an angle of 60·4°

Table 4. *Interatomic distances and bond angles with their e.s.d.'s*

C(1)—C(2)	1·389 (6) Å	C(3)–C(4)—C(5)	119·6 (5)°
C(2)—C(3)	1·378 (7)	C(4)–C(5)—C(6)	120·4 (4)
C(3)—C(4)	1·380 (7)	C(1)–C(6)—C(5)	119·2 (4)
C(4)—C(5)	1·405 (7)	C(2)–C(1)—C(6)	120·2 (4)
C(5)—C(6)	1·390 (6)	C(1)–C(6)—C(11)	122·6 (4)
C(1)—C(6)	1·385 (6)	C(5)–C(6)—C(11)	118·2 (4)
C(6)—C(11)	1·524 (6)	C(6)–C(11)–N(1)	114·3 (3)
N(1)—C(11)	1·476 (5)	C(7)–N(1)—C(11)	113·8 (3)
N(1)—C(7)	1·458 (5)	N(1)–C(7)—C(8)	110·2 (3)
C(7)—C(8)	1·525 (5)	N(1)–C(7)—C(9)	118·7 (3)
C(7)—C(9)	1·536 (5)	C(8)–C(7)—C(9)	103·5 (3)
C(9)—C(10)	1·508 (5)	C(7)–C(8)—N(2)	109·0 (3)
C(8)—O(1)	1·219 (5)	C(7)–C(8)—O(1)	126·0 (3)
C(10)–O(2)	1·202 (5)	N(2)–C(8)—O(1)	125·0 (4)
C(8)—N(2)	1·358 (5)	C(8)–N(2)—C(10)	113·2 (3)
C(10)–N(2)	1·384 (5)	N(2)–C(10)–C(9)	108·5 (3)
		N(2)–C(10)–O(2)	124·5 (4)
C(1)—C(2)—C(3)	120·7 (4)°	C(9)–C(10)–O(2)	127·0 (4)
C(2)—C(3)—C(4)	120·0 (5)	C(7)–C(9)—C(10)	104·7 (3)

Table 5. *Least-squares planes*

The equation of the plane through the carbon atoms of the phenyl ring

$$\text{I}: \; -0{\cdot}4407X + 0{\cdot}4621Y + 0{\cdot}7696Z = 4{\cdot}0236$$

The equations of the planes through the atoms of the succinimide moiety

$$\text{II}a: \; -0{\cdot}5783X - 0{\cdot}5242Y + 0{\cdot}6252Z = 0{\cdot}9187$$

$$\text{II}b: \; -0{\cdot}5476X - 0{\cdot}5516Y + 0{\cdot}6292Z = 1{\cdot}0273$$

Distances (Å) from the planes

	Plane I	Plane II*a*	Plane II*b*
C(1)	0·007*		
C(2)	−0·003*		
C(3)	−0·006*		
C(4)	0·010*		
C(5)	−0·006*		
C(6)	−0·003*		
C(7)		−0·062*	−0·091*
C(8)		0·049*	−0·009*
C(9)		0·055*	0·087*
C(10)		−0·029*	0·005*
N(2)		−0·014*	−0·033*
O(1)		0·161	0·054*
O(2)		−0·089	−0·013*
H(1)	0·048		
H(2)	0·089		
H(3)	0·148		
H(4)	−0·169		
H(5)	−0·094		
H(7)		−1·006	−1·043
H(91)		0·957	1·006
H(92)		−0·605	−0·548
H(N2)		−0·027	−0·050
Angle with plane I		60·4°	61·9°

* Atoms defining the plane.

with that of the phenyl group (Table 5) in which the mean bond length is 1·388 Å. N(1) is bound to two sp^3 carbon atoms, and is thus forced to preserve its own sp^3 character which is shown by the C–N single bonds [1·458 (5) and 1·476 (5) Å] and the sum of the bond angles (345·2°) around it.

The presence of the water molecule alters the characteristic hydrogen bonding of the succinimide rings found in the dimers of the PH-PD(*o*) and PHA-PD derivatives. Even the weak hydrogen bond (type N–H···O) which is formed within the PHA-PD molecule (2·90 and 2·47 Å) does not exist (its present parameters: N(1)···O(1) = 2·90 Å, H(N1)···O(1) = 2·73 Å, N–H–O = 87·7°).

As was revealed in the course of the location of the missing hydrogen atoms, each watei molecule is surrounded by four molecules of BA-PD (Fig. 2) from which one O(1) and N(1) and two N(2) atoms participate in the formation of four hydrogen bonds (Table 6). In two of these the oxygen atom of the water molecule *W*(1) acts as donor, and in the other two as acceptor. The O–H···N(2) bond is rather weak, which is understandable, since N(2) also forms a strong N–H···O bond with the oxygen of the water molecule *W*(2) sitting above *W*(1) at a distance of $z=0{\cdot}5$. The water molecules sitting above each other at a distance of $z=0{\cdot}5$ have identical x and slightly different y ($\Delta y=0{\cdot}038$) fractional coordinates. This geometry can be expressed by a pseudo-4_1 axis which runs through the O(*W*) atoms at $y=\frac{1}{4}$. Its unit is the doubled c axis. Thus the infinite channel around the 4_1 axis contains 16 hydrogen bonds per unit. The water molecules are linked together by the hydrogen bonds formed by the atoms N(2) of the succinimide rings. The neighbouring channels of the water molecules have of course 4_3 symmetries.

Table 6. *Hydrogen bonds formed by the oxygen atom of the water molecule*

		X–H	X···H	H···Y	X–H–Y
[1]	N(2′)–H···O(*W*)	0·92 Å	2·81 Å	1·89 Å	175·4°
[2]	N(1)—H···O(*W*)	1·10	2·88	1·78	172·4
[3]	O(*W*)–H···O(1)	0·87	2·92	2·12	152·0
[4]	O(*W*)–H···N(2″)*	0·68	3·26	2·65	152·3

* This can be regarded as a rather weak hydrogen bond, the acceptor of which, N(2), forms the hydrogen bonds of type [1] with the O(*W*) at $x,\frac{1}{2}-y,\frac{1}{2}+z$.

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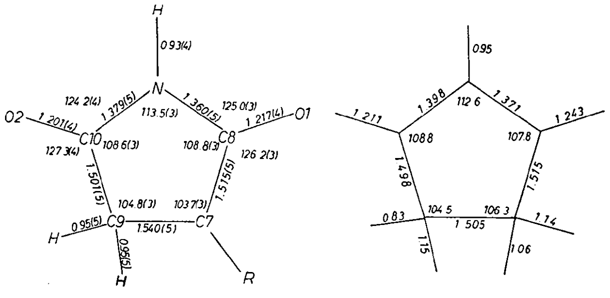

Fig. 1. Mean values of the dimensions of the succinimide ring for (*a*) PH–PD(*o*), BA–PD, PHA–PD and (*b*) succinimide (Mason, 1961).

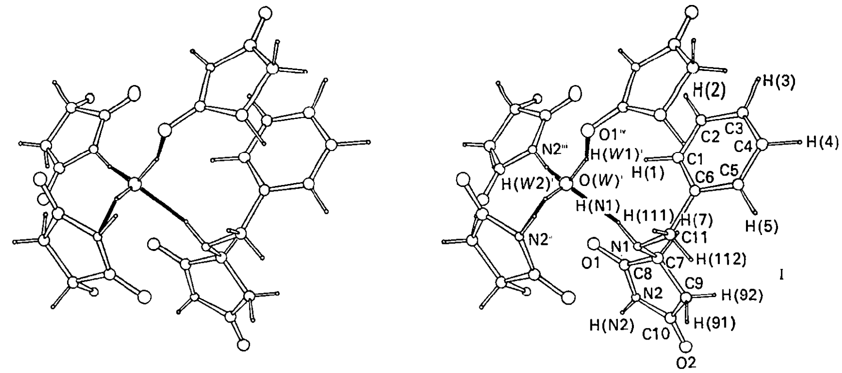

Fig. 2. Stereoscopic (*ORTEP*) diagram of the molecular packing. The water molecule *W*(1) is surrounded by four molecules of the succinimide derivative (i–iv).

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Anion Ordering in TaON: A Powder Neutron-Diffraction Investigation

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The structure of tantalum oxynitride has been determined by the profile analysis of powder neutron-diffraction data collected at 4·2°K. The compound is monoclinic, space group $P2_1/c$, with $a=4{\cdot}9581$, $b=5{\cdot}0267$, $c=5{\cdot}1752$ Å, and $\beta=99{\cdot}640°$ (4·2°K). Complete ordering of the anions occurs in alternate layers normal to the [100] direction and this ordering is consistent with calculated site potentials. Short nitrogen–nitrogen distances of 2·51 to 2·64 Å are observed.

Introduction

Two polymorphs have been reported for TaON: a red low-temperature form with a complex hexagonal structure (Buslaev, Glushkova, Ershova & Shustorovich, 1966; Buslaev *et al.*, 1969) which transforms at approximately 800°C to a green modification, first reported by Brauer & Weidlein (1965) and Brauer, Weidlein & Strahle (1966). The latter has a monoclinic structure and is probably isostructural with baddeleyite (ZrO_2). Mixed anion compounds, including oxyfluorides, *e.g.* YOF (Mann & Bevan 1970), are often ordered in layers and oxynitrides may be similarly ordered. The difference in the neutron scattering lengths for oxygen and nitrogen allows this problem to be solved by the analysis of the diffraction profile obtained from neutron powder data.

Experimental

TaON was prepared by a method similar to that of Brauer *et al.* (1966). 'Specpure' grade Ta_2O_5, supplied by Johnson Matthey Chemicals Ltd, was heated to 830°C in a flow of dry ammonia until the weight change, colour and X-ray Debye-Scherrer photographs indicated complete conversion to TaON according to the equation

$$Ta_2O_5+2NH_3 \rightarrow 2TaON+3H_2O\,.$$

The product was analysed by reconversion to Ta_2O_5 in flowing oxygen on a thermogravimetric balance. Two separate determinations gave compositions of $TaO_{0\cdot98\,(2)}N_{1\cdot01\,(2)}$ and $TaO_{1\cdot01\,(2)}N_{0\cdot99\,(2)}$. Attempts to alter the O:N ratio on the oxygen-rich side of TaON gave a mixture of phases and Swisher & Read (1972) report that the non-stoichiometric range of TaON extends only to the nitrogen-rich side.

A room-temperature X-ray diffractometer trace was indexed on a monoclinic unit cell and a least-squares determination of the unit-cell parameters gave $a=4{\cdot}9692$ (3) (4·966), $b=5{\cdot}0330$ (3) (5·034), $c=5{\cdot}1821$ (3) (5·185) Å and $\beta=99{\cdot}682$ (5)° (99·65) where the Brauer *et al.* (1966) values are in parentheses. The systematic absences ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$) indicate the space group $P2_1/c$.

Neutron-diffraction measurements were carried out on the PANDA powder diffractometer at AERE Harwell. The sample was contained in a thin-walled vanadium can which was suspended in a liquid-helium cryostat. A neutron wavelength of 1·537 Å [obtained by reflexion from the (331) planes of a germanium monochromator at a take-off angle of 72°] was employed and the diffraction pattern recorded from 12 to 85° (2θ) in steps of 0·02°.

Results

The neutron-diffraction profile contained 91 reflexions consistent with $P2_1/c$. Refinements were carried out by means of a least-squares comparison of observed and calculated profiles (Rietveld, 1969). The program minimizes the function $\chi^2=\sum_i w_i[y_i(\text{obs})-1/cy_i(\text{calc})]^2$