

$S = 1.20$   
1918 reflections  
226 parameters  
 $w = 1/[\sigma^2(F) + 0.0046F^2]$

Extinction correction: none  
Atomic scattering factors  
from *SHELXTL-Plus*  
(Sheldrick, 1991)

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.  
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Revision 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
Siemens (1994). *P3 Software*. Version 4.21. Siemens Analytical Software, Madison, Wisconsin, USA.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Cl	0.5860 (1)	0.0743 (1)	0.6893 (1)	0.063 (1)
N1	1.1076 (2)	0.0459 (3)	0.3806 (2)	0.040 (1)
N2	0.6772 (2)	0.0015 (3)	0.1805 (2)	0.039 (1)
N3	0.6020 (2)	-0.0989 (3)	0.0418 (2)	0.043 (1)
O1	0.8395 (2)	0.2511 (3)	0.4049 (3)	0.068 (1)
C1	0.9709 (3)	-0.0616 (4)	0.2646 (3)	0.045 (1)
C2	1.0173 (3)	0.0369 (4)	0.3436 (3)	0.035 (1)
C3	0.9739 (2)	0.1411 (4)	0.3900 (3)	0.033 (1)
C4	0.8785 (3)	0.1600 (4)	0.3654 (3)	0.042 (2)
C5	0.8265 (3)	0.0565 (5)	0.2875 (4)	0.063 (2)
C6	0.8775 (3)	-0.0118 (7)	0.2143 (5)	0.052 (2)
C7	1.0430 (2)	0.2184 (4)	0.4584 (3)	0.034 (1)
C8	1.0434 (3)	0.3321 (4)	0.5235 (3)	0.043 (1)
C9	1.1246 (3)	0.3829 (4)	0.5761 (3)	0.051 (2)
C10	1.2058 (3)	0.3218 (4)	0.5665 (3)	0.050 (2)
C11	1.2082 (2)	0.2060 (4)	0.5047 (3)	0.045 (1)
C12	1.1254 (2)	0.1559 (4)	0.4504 (3)	0.035 (1)
C13	0.7307 (3)	0.0995 (4)	0.2505 (3)	0.047 (1)
C14	0.6461 (3)	-0.1222 (5)	0.2134 (3)	0.051 (1)
C15	0.5999 (3)	-0.1843 (5)	0.1275 (3)	0.053 (2)
C16	0.6487 (2)	0.0127 (4)	0.0746 (3)	0.038 (1)
C17	0.6649 (3)	0.1293 (5)	0.0053 (4)	0.057 (2)
C18	1.1769 (3)	-0.0492 (5)	0.3564 (4)	0.062 (2)
O1W	0.4759 (2)	0.1486 (4)	0.1618 (2)	0.076 (1)
O2W	0.3919 (2)	0.5064 (5)	0.0536 (3)	0.094 (2)

*Acta Cryst.* (1995). C51, 2629–2633

## Molecular Co-Crystals of Carboxylic Acids. 22.† The Adducts of Pyrazine-2,3-dicarboxylic Acid with 2-Aminobenzoic Acid (1:2) and 3-Aminobenzoic Acid (1:1 Dihydrate)

GRAHAM SMITH\* AND DANIEL E. LYNCH

*School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane 4001, Australia*

KARL A. BYRIEL AND COLIN H. L. KENNARD

*Department of Chemistry, The University of Queensland, Brisbane 4072, Australia*

(Received 13 December 1994; accepted 19 June 1995)

Table 2. *Hydrogen-bonding geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O1W—H1W1···Cl <sup>i</sup>	0.862 (5)	2.299 (4)	3.160 (4)	177.2 (4)
O1W—H2W1···Cl <sup>ii</sup>	0.965 (5)	2.243 (4)	3.176 (4)	162.4 (3)
O2W—H1W2···Cl <sup>iii</sup>	1.269 (5)	2.135 (4)	3.226 (4)	141.4 (3)
O2W—H2W2···Cl <sup>iiii</sup>	0.872 (6)	2.402 (4)	3.264 (4)	170.3 (5)
N3—H3···O1W <sup>v</sup>	0.900 (4)	1.800 (4)	2.699 (4)	178.7 (4)

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

H-atoms were located from difference Fourier maps and included as riding atoms with fixed isotropic displacement parameters in the structure-factor calculations.

Data collection: Siemens (1994) *P3 Software*. Cell refinement: *P3 Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983).

This work was supported by the Council of Scientific and Industrial Research, India.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

## References

Bozigian, H. P., Pritchard, J. F., Gooding, A. E. & Pakes, G. E. (1994). *J. Pharm. Sci.* 83, 1011–1013.

## Abstract

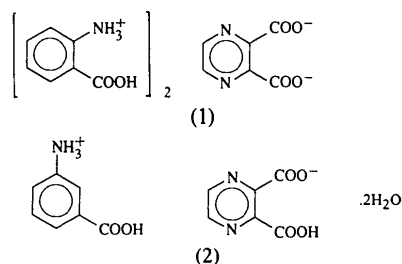
The structures of two molecular adducts of pyrazine-2,3-dicarboxylic acid (PDCA) with the carboxylic acids 2-aminobenzoic acid (2-ABA), *i.e.* bis(2-carboxyphenylammonium) 2,3-pyrazinedicarboxylate, [(PDCA)<sup>2-</sup>(2-ABA<sup>+</sup>)<sub>2</sub>], (1), and 3-aminobenzoic acid (3-ABA), *i.e.* 3-carboxyphenylammonium hydrogen 2,3-pyrazinedicarboxylate dihydrate, [(PDCA)(3-ABA)<sup>+</sup>·2H<sub>2</sub>O], (2), have been determined by X-ray diffraction. In adduct (1), each carboxylic acid group of PDCA protonates an amino group of a two 2-ABA molecule. The ion pairs then associate *via* hydrogen bonding giving a three-dimensional network structure. In (2), a single proton transfer occurs. The protonated amine group of 3-ABA then forms hydrogen bonds with the carboxylate O atoms and the hetero N atom of PDCA as well as with the water molecules. The two 3-ABA molecules also associate to form a cyclic hydrogen-bonded dimer. This results in a three-dimensional network structure.

## Comment

The aromatic heterocyclic dicarboxylic acid pyrazine-2,3-dicarboxylic (PDCA) provides an example of a proton-donor molecule which has the potential to give

† Part 21: Smith, Gentner, Lynch, Byriel & Kennard (1995).

both (1:1) or (1:2) molecular adducts with suitable acceptor systems. In addition, the presence of *ortho*-related N atoms in the hetero ring should result in stabilization of the co-crystal intermolecular hydrogen-bonding associations. However, in the structures of the adducts of PDCA reported to date, only (1:1) associations have been found; this appears to be preferred for dicarboxylic acids, at least with nitrogen-base proton-acceptor systems, *e.g.* 2-aminopyrimidine (Etter & Adsmund, 1990). The three reported structures of PDCA are with the bases 3-hydroxypyridine and 3-amino-1*H*-1,2,4-triazole and with the bifunctional acid 4-aminobenzoic acid (4-ABA) (Lynch, Smith, Byriel, Kennard & Whittaker, 1994). To complete the series of adducts of PDCA with other isomeric monoamino carboxylic acids, the 1:2 complex of PDCA with 2-aminobenzoic acid (anthranilic acid; 2-ABA), [(PDCA)(2-ABA)<sub>2</sub>], (1), was prepared in 95% aqueous ethanol using previously described procedures (Lynch *et al.*, 1994). However, initial attempts to prepare a crystalline adduct of PDCA with 3-aminobenzoic acid (3-ABA) from ethanol were unsuccessful. Subsequent use of 50% aqueous ethanol gave co-crystals, found to be the 1:1 adduct hydrate, [(PDCA)(3-ABA)·2H<sub>2</sub>O], (2). The structures of these complexes were determined to enable the hydrogen-bonding modes to be described.



The structure of complex (1) involves the transfer of both carboxylic acid protons of the PDCA (molecule A) to the amino groups of the two 3-ABA molecules [molecules B and B<sup>1</sup>; symmetry code: (i) 1-x, y,  $\frac{3}{2}-z$ ]. These are related by crystallographically imposed twofold rotational symmetry, which also bisects the PDCA molecule (Fig. 1). The carboxylate groups of this molecule are not coplanar with the pyrazine ring [N(1A)—C(2A)—C(21A)—O(20A) -129.1 (2)°, compared with 145.4° in the parent acid (Takusagawa & Shimada, 1973), and -178.0 and 174.6° in the 1:1 adduct of PDCA with 3-amino-1*H*-1,2,4-triazole (Lynch *et al.*, 1994)]. The protonated amine group is subsequently involved in a number of intermolecular hydrogen-bonding associations (Fig. 2) with a carboxyl O atom: N(3B)—H(32B)···O(20A) ( $-\frac{1}{2}+x, -\frac{1}{2}+y, \frac{3}{2}-z$ ) 2.754 (2) Å, 157 (2)°; N(3B)—H(33B)···O(21A) ( $\frac{1}{2}-x, -\frac{1}{2}-y, 1-z$ ) 2.738 (2)°, 166 (3)°; N(3B)—H(31B)···O(10B) ( $-x, -y, 1-z$ ) 3.182 (2) Å, 132 (2)°. In addition, an intramolecular hydrogen bond is found in the 2-ABA mol-

ecule between the amino group and the carboxyl O atom [N(3B)—H(31B)···O(10B) 2.694 (2) Å, 143 (2)°], similar to that found in all polymorphs of the parent acid (Brown, 1968; Khan & Srivastava, 1968; Boone, Derissen & Schoone, 1977; Hardy, Kaska, Chandra & Zink, 1981). This maintains approximate planarity in the molecule [torsion angle C(2B)—C(1B)—C(11B)—O(11B) 169.3 (3)°]. A single strong hydrogen bond links this carboxyl group to PDCA [O(11B)—H(11B)···O(21A) ( $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$ ) 2.550 (2) Å, 162 (4)°], completing a three-centre bonding arrangement about O(21A) and forming a ribbon-polymer structure extending along the c cell direction (Fig. 2).

The structure of the 1:1 complex hydrate [(PDCA)(3-ABA)·2H<sub>2</sub>O], (2) (Figs. 3 and 4), comprises amine-protonated 3-ABA molecules (molecule B) which form

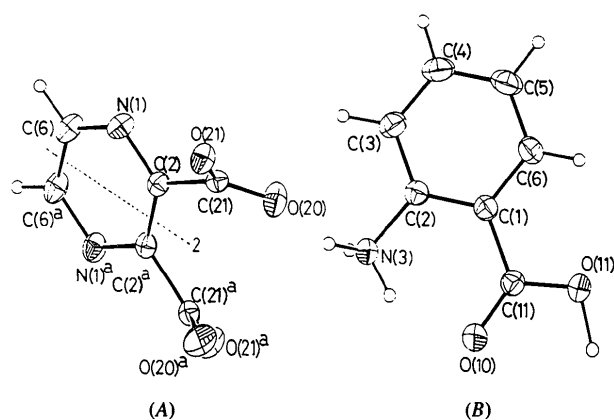


Fig. 1. Molecular conformation and atom-numbering scheme for the individual molecules in the adduct [(PDCA)(2-ABA)<sub>2</sub>], (1). H atoms take the number of the attached atom. Displacement ellipsoids are plotted at the 50% probability level.

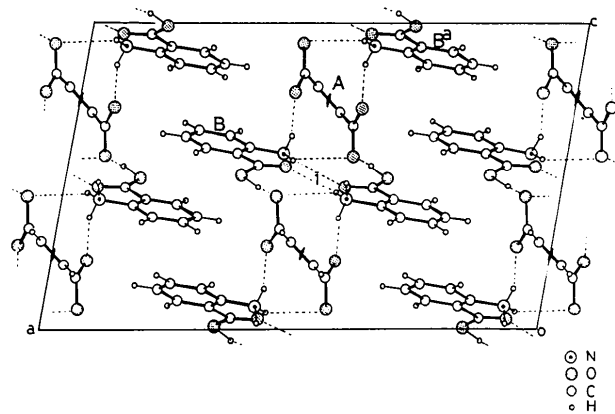


Fig. 2. Packing of the molecular adduct [(PDCA)(2-ABA)<sub>2</sub>] in the unit cell. Hydrogen bonds are shown as broken lines.

centrosymmetric hydrogen-bonded cyclic dimers, (8) (graph set  $R_2^2$ ; Etter, 1990) [O(11B)—H(11B)···O(10B) ( $1-x, 1-y, 1-z$ ) 2.622 (2) Å, 175 (4)°], similar to those found in the majority of carboxylic acids (Leiserowitz, 1976). The three protons of the ammonium group of 3-ABA are then involved in a total of five hydrogen-bonding interactions with the PDCA molecule (molecule A) and with the lattice waters. The first proton [H(31B)] forms a three-centre association with a hetero N atom and a carboxylic O atom of PDCA [N(3B)—H(31B)···N(4A) ( $-1+x, -1+y, z$ ) 3.120 (3) Å, 131 (2)°; N(3B)—H(31B)···O(30A) ( $-1+x, -1+y, z$ ) 2.824 (3) Å, 150 (2)°]. The second proton [H(32B)] is also linked to O(30A) [2.824 (3) Å, 150 (2)°] and to a single water molecule [N(3B)—H(32B)···OW(1) ( $-x, -y, 1-z$ ) 2.860 (3) Å, 99 (2)°]. The third proton [H(33B)] is also three-centred, being linked to two symmetry-related OW(1) water molecules [N(3B)—H(33B)···OW(1) ( $x, y, -1+z$ ) 2.952 (3) Å, 124 (3)°; N(3B)—H(33B)···OW(1) ( $-x, y, 1-z$ ) 2.860 (3) Å, 147 (3)°]. Both lattice waters are also involved in a number of hydrogen bonds to PDCA carboxyl O atoms and hetero N atoms. These are: OW(1)—H(11)···O(21A) ( $x, y, 1+z$ ) 2.844 (3) Å, 172 (3)°; OW(1)—H(12)···O(21A) ( $1-x, -y, 1-z$ ) 2.984 (3) Å, 139 (4)°; OW(1)—H(12)···N(1A) ( $1-x, -y, 1-z$ ) 2.974 (3) Å, 151 (4)°; OW(2)—H(21)···O(30A) 3.064 (3) Å, 144 (4)°; OW(2)—H(21)···O(31A) 3.117 (3) Å, 139 (4)°; OW(2)—H(22)···O(21A) ( $1-x, 1-y, -z$ ) 3.275 (3) Å, 144 (5)°. The result is a layer structure stacking down the approximate  $c$  cell direction with a complex network of hydrogen bonds linking the homo dimers of 3-ABA from the primary association with PDCA molecules and water molecules between and across the layers. The 3-ABA molecules are similar in conformation to the parent acid (Voogd, Verzijl & Duisenberg, 1980), with the carboxylic group only slightly out of the plane of the benzene ring [torsion angle C(2B)—C(1B)—C(11B)—O(10B) 165.9 (2)°, *cf.*  $-177.8^\circ$  in the parent acid].

The PDCA ion is planar in this adduct, largely due to the involvement of the single proton in the intramolecular hydrogen bond between the carboxylic acid groups [O(31)—H(31)···O(20) 2.377 (3) Å]. The torsion angles N(1A)—C(2A)—C(21A)—O(20A) and N(4A)—C(3A)—C(31A)—O(31A) in (2) are  $-173.6$  (3) and  $179.7$  (3)°, respectively, while the analogous value in the parent acid where the two groups are related by twofold rotational symmetry is  $145.4^\circ$  (Takusagawa & Shimada, 1973). Similar hydrogen-bonding relationships are found for the adducts of PDCA with 4-aminobenzoic acid and 3-amino-1*H*-1,2,4-triazole, but not with 3-hydroxypyridine (Lynch *et al.*, 1994), or compound (1), where both carboxyl groups are deprotonated. For compound (1), the carboxyl groups are synclinally related [torsion angle N(1A)—C(2A)—C(21A)—O(21A)  $49.1$  (2)°].

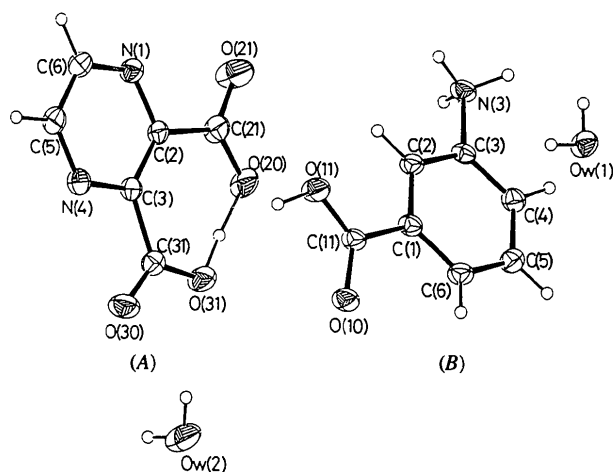


Fig. 3. Molecular conformation and atom-numbering scheme for the individual molecules in the adduct [(PDCA)(3-ABA).2H<sub>2</sub>O], (2). H atoms take the number of the attached atom. Displacement ellipsoids are plotted at the 50% probability level.

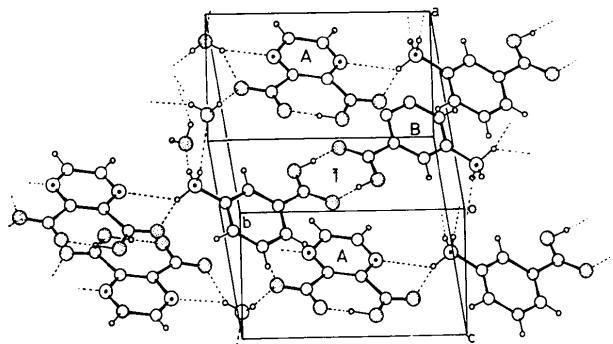


Fig. 4. Perspective view of the packing of the molecular adduct [(PDCA)(3-ABA).2H<sub>2</sub>O] in the unit cell.

## Experimental

Compound (1) was prepared by refluxing equimolar amounts of pyrazine-2,3-dicarboxylic acid and 2-aminobenzoic acid (anthranilic acid) in 95% aqueous ethanol for 20 min at 383 K. Pale brown prisms (m.p. 441–443 K) formed upon total evaporation of the solvent at room temperature. Compound (2) was prepared by refluxing equimolar amounts of pyrazine-2,3-dicarboxylic acid and 3-aminobenzoic acid in 50% aqueous ethanol for 20 min at 383 K. Pale brown prisms (m.p. 461–462 K) formed upon total evaporation of the solvent at room temperature.

### Compound (1)

#### Crystal data

$2C_7H_8NO_2^+ \cdot C_6H_2N_2O_4^{2-}$   
 $M_r = 442.4$   
 Monoclinic  
 $C2/c$   
 $a = 20.934$  (4) Å  
 $b = 7.6360$  (4) Å  
 $c = 12.966$  (2) Å  
 $\beta = 100.250$  (8)°

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 6-14^\circ$

$\mu = 0.144$  mm<sup>-1</sup>

$T = 293$  (2) K

Plate

$V = 2039.6(5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.441 \text{ Mg m}^{-3}$

$0.40 \times 0.30 \times 0.20 \text{ mm}$   
 Brown

O(21A)—C(21A)—C(2A) 115.6 (2) C(2B)—C(3B)—C(4B) 119.4 (2)  
 N(1A)—C(6A)—C(6A') 122.06 (11) C(5B)—C(4B)—C(3B) 120.0 (2)  
 C(2B)—C(1B)—C(6B) 117.8 (2) C(4B)—C(5B)—C(6B) 120.6 (2)  
 C(2B)—C(1B)—C(11B) 122.0 (2) C(5B)—C(6B)—C(1B) 120.6 (2)  
 C(6B)—C(1B)—C(11B) 120.2 (2)

Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1870 measured reflections  
 1791 independent reflections  
 1351 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -4 \rightarrow 24$   
 $k = 0 \rightarrow 9$   
 $l = -15 \rightarrow 15$   
 3 standard reflections  
 monitored every 250  
 reflections  
 intensity decay: 1%

### Compound (2)

#### Crystal data

C<sub>7</sub>H<sub>8</sub>NO<sub>2</sub><sup>+</sup>·C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>O<sub>4</sub><sup>-</sup>·2H<sub>2</sub>O  
 $M_r = 341.3$   
 Triclinic  
 P1  
 $a = 7.892(1) \text{ \AA}$   
 $b = 9.490(2) \text{ \AA}$   
 $c = 10.115(2) \text{ \AA}$   
 $\alpha = 91.830(1)^\circ$   
 $\beta = 91.460(1)^\circ$   
 $\gamma = 100.350(2)^\circ$   
 $V = 744.5(2) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.522 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 6-14^\circ$   
 $\mu = 0.128 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Prismatic  
 $0.35 \times 0.24 \times 0.12 \text{ mm}$   
 Pale brown

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.033$   
 $wR(F^2) = 0.097$   
 $S = 0.62$   
 1351 reflections  
 181 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.139P)^2 + 3.55P]$   
 where  $P = [\max(F_o^2, 0) + 2(F_o^2)]/3$

$(\Delta/\sigma)_{\text{max}} < 0.01$   
 $\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 4617 measured reflections  
 4325 independent reflections  
 2193 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 30^\circ$   
 $h = 0 \rightarrow 11$   
 $k = -13 \rightarrow 13$   
 $l = -14 \rightarrow 14$   
 3 standard reflections  
 monitored every 250  
 reflections  
 intensity decay: 2.6%

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (1)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
N(1A)	0.4456 (1)	-0.3111 (2)	0.6701 (1)	0.043 (1)
C(2A)	0.4730 (1)	-0.1626 (2)	0.7097 (1)	0.033 (1)
C(21A)	0.4416 (1)	0.0057 (2)	0.6657 (1)	0.034 (1)
O(20A)	0.4283 (1)	0.1184 (2)	0.7257 (1)	0.053 (1)
O(21A)	0.4295 (1)	0.0162 (2)	0.5667 (1)	0.046 (1)
C(6A)	0.4729 (1)	-0.4593 (3)	0.7112 (2)	0.046 (1)
C(1B)	0.1655 (1)	-0.0435 (2)	0.5766 (1)	0.037 (1)
C(11B)	0.1201 (1)	0.1019 (3)	0.5370 (2)	0.038 (1)
O(10B)	0.0618 (1)	0.0928 (2)	0.5329 (1)	0.050 (1)
O(11B)	0.1486 (1)	0.2394 (2)	0.5063 (2)	0.063 (1)
C(2B)	0.1434 (1)	-0.2094 (3)	0.5966 (1)	0.036 (1)
C(3B)	0.1858 (1)	-0.3430 (3)	0.6335 (2)	0.049 (1)
N(3B)	0.0739 (1)	-0.2517 (2)	0.5768 (1)	0.037 (1)
C(4B)	0.2519 (1)	-0.3117 (4)	0.6508 (2)	0.058 (1)
C(5B)	0.2748 (1)	-0.1489 (4)	0.6315 (2)	0.058 (1)
C(6B)	0.2326 (1)	-0.0156 (3)	0.5943 (2)	0.049 (1)

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.046$   
 $wR(F^2) = 0.119$   
 $S = 1.00$   
 2193 reflections  
 278 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.04P]$   
 where  $P = [\max(F_o^2, 0) + 2(F_o^2)]/3$

$(\Delta/\sigma)_{\text{max}} = 0.1$   
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

N(1A)—C(2A)	1.331 (2)	C(1B)—C(11B)	1.492 (3)
N(1A)—C(6A)	1.336 (3)	C(11B)—O(10B)	1.214 (2)
C(2A)—C(2A')	1.398 (4)	C(11B)—O(11B)	1.305 (2)
C(2A)—C(21A)	1.509 (2)	C(2B)—C(3B)	1.381 (3)
C(21A)—O(20A)	1.225 (2)	C(2B)—N(3B)	1.469 (2)
C(21A)—O(21A)	1.266 (2)	C(3B)—C(4B)	1.382 (3)
C(6A)—C(6A')	1.375 (4)	C(4B)—C(5B)	1.372 (4)
C(1B)—C(2B)	1.389 (3)	C(5B)—C(6B)	1.377 (3)
C(1B)—C(6B)	1.398 (3)		
C(2A)—N(1A)—C(6A)	116.3 (2)	O(10B)—C(11B)—O(11B)	122.9 (2)
N(1A)—C(2A)—C(2A')	121.61 (10)	O(10B)—C(11B)—C(1B)	123.1 (2)
N(1A)—C(2A)—C(21A)	116.8 (2)	O(11B)—C(11B)—C(1B)	114.0 (2)
C(2A')—C(2A)—C(21A)	121.54 (9)	C(3B)—C(2B)—C(1B)	121.6 (2)
O(20A)—C(21A)—O(21A)	125.0 (2)	C(3B)—C(2B)—N(3B)	117.0 (2)
O(20A)—C(21A)—C(2A)	119.4 (2)	C(1B)—C(2B)—N(3B)	121.4 (2)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
N(1A)	0.8367 (2)	0.2951 (2)	0.1053 (2)	0.041 (1)
C(2A)	0.7099 (2)	0.3685 (2)	0.1300 (2)	0.035 (1)
C(3A)	0.7497 (2)	0.5120 (2)	0.1762 (2)	0.034 (1)
N(4A)	0.9150 (2)	0.5761 (2)	0.1981 (2)	0.043 (1)
C(5A)	1.0372 (3)	0.5004 (2)	0.1744 (2)	0.045 (1)
C(6A)	0.9985 (3)	0.3600 (2)	0.1268 (2)	0.044 (1)
C(21A)	0.5321 (3)	0.2758 (2)	0.1008 (2)	0.051 (1)
O(20A)	0.3981 (2)	0.3316 (2)	0.1070 (2)	0.062 (1)
O(21A)	0.5258 (3)	0.1512 (2)	0.0706 (3)	0.108 (1)

C(31A)	0.6267 (3)	0.6144 (2)	0.2100 (2)	0.044 (1)
O(30A)	0.6866 (2)	0.7353 (2)	0.2522 (2)	0.062 (1)
O(31A)	0.4650 (2)	0.5708 (2)	0.1955 (2)	0.068 (1)
C(1B)	0.1412 (2)	0.2520 (2)	0.4240 (2)	0.035 (1)
C(2B)	0.1530 (3)	0.1295 (2)	0.3481 (2)	0.036 (1)
C(3B)	0.0036 (2)	0.0338 (2)	0.3145 (2)	0.035 (1)
N(3B)	0.0135 (3)	-0.0907 (2)	0.2275 (2)	0.042 (1)
C(4B)	-0.1549 (3)	0.0553 (2)	0.3562 (2)	0.041 (1)
C(5B)	-0.1649 (3)	0.1765 (2)	0.4338 (2)	0.045 (1)
C(6B)	-0.0171 (3)	0.2753 (2)	0.4669 (2)	0.041 (1)
O(10B)	0.2840 (2)	0.4812 (1)	0.5022 (2)	0.050 (1)
O(11B)	0.4443 (2)	0.3223 (2)	0.4372 (2)	0.054 (1)
C(11B)	0.2992 (2)	0.3597 (2)	0.4575 (2)	0.038 (1)
OW(1)	0.1904 (2)	0.0097 (2)	0.9851 (2)	0.050 (1)
OW(2)	0.3627 (3)	0.8709 (3)	0.2380 (3)	0.082 (1)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

N(1A)—C(6A)	1.323 (3)	C(31A)—O(31A)	1.272 (3)
N(1A)—C(2A)	1.342 (2)	C(1B)—C(6B)	1.385 (3)
C(2A)—C(3A)	1.403 (3)	C(1B)—C(2B)	1.392 (3)
C(2A)—C(21A)	1.533 (3)	C(1B)—C(11B)	1.487 (3)
C(3A)—N(4A)	1.347 (2)	C(2B)—C(3B)	1.380 (3)
C(3A)—C(31A)	1.529 (3)	C(3B)—C(4B)	1.377 (3)
N(4A)—C(5A)	1.323 (3)	C(3B)—N(3B)	1.466 (2)
C(5A)—C(6A)	1.381 (3)	C(4B)—C(5B)	1.387 (3)
C(21A)—O(21A)	1.204 (3)	C(5B)—C(6B)	1.385 (3)
C(21A)—O(20A)	1.267 (3)	O(10B)—C(11B)	1.252 (2)
C(31A)—O(30A)	1.219 (3)	O(11B)—C(11B)	1.277 (2)
C(6A)—N(1A)—C(2A)	118.8 (2)	O(31A)—C(31A)—C(3A)	119.4 (2)
N(1A)—C(2A)—C(3A)	120.1 (2)	C(6B)—C(1B)—C(2B)	120.4 (2)
N(1A)—C(2A)—C(21A)	111.4 (2)	C(6B)—C(1B)—C(11B)	119.9 (2)
C(3A)—C(2A)—C(21A)	128.5 (2)	C(2B)—C(1B)—C(11B)	119.7 (2)
N(4A)—C(3A)—C(2A)	120.2 (2)	C(3B)—C(2B)—C(1B)	118.5 (2)
N(4A)—C(3A)—C(31A)	111.1 (2)	C(4B)—C(3B)—C(2B)	121.9 (2)
C(2A)—C(3A)—C(31A)	128.7 (2)	C(4B)—C(3B)—N(3B)	119.2 (2)
C(5A)—N(4A)—C(3A)	118.2 (2)	C(2B)—C(3B)—N(3B)	118.9 (2)
N(4A)—C(5A)—C(6A)	121.6 (2)	C(3B)—C(4B)—C(5B)	119.2 (2)
N(1A)—C(6A)—C(5A)	120.9 (2)	C(6B)—C(5B)—C(4B)	120.1 (2)
O(21A)—C(21A)—O(20A)	122.2 (2)	C(1B)—C(6B)—C(5B)	120.0 (2)
O(21A)—C(21A)—C(2A)	117.9 (2)	O(10B)—C(11B)—O(11B)	123.6 (2)
O(20A)—C(21A)—C(2A)	119.9 (2)	O(10B)—C(11B)—C(1B)	119.1 (2)
O(30A)—C(31A)—O(31A)	121.7 (2)	O(11B)—C(11B)—C(1B)	117.3 (2)
O(30A)—C(31A)—C(3A)	118.9 (2)		

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least squares with anisotropic displacement parameters for all non-H atoms. H-atom positions were located by difference methods and included in the respective refinements with both positional and isotropic displacement parameters refined.

For both compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal3.2* (Hall, Flack & Stewart, 1992); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON92* (Spek, 1990).

The authors acknowledge financial assistance from the Australian Research Council, The University of Queensland and the Centre for Instrumental and Developmental Chemistry of the Queensland University of Technology.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Boone, C. D. G., Derissen, J. L. & Schoone, J. C. (1977). *Acta Cryst.* B33, 3205–3206.
- Brown, C. J. (1968). *Proc. R. Soc. A*, **302**, 185–199.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Etter, M. C. & Admond, D. A. (1990). *J. Chem. Soc. Chem. Commun.* pp. 589–591.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Hall, S. R., Flack, H. D. & Stewart, S. J. (1992). *Xtal3.2 Reference Manual*. Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Hardy, G. E., Kaska, W. C., Chandra, B. P. & Zink, J. I. (1981). *J. Am. Chem. Soc.* **103**, 1074–1079.
- Khan, M. Y. & Srivastava, P. (1968). *Ind. J. Pure Appl. Phys.* **6**, 166–170.
- Leiserowitz, L. (1976). *Acta Cryst.* B32, 775–802.
- Lynch, D. E., Smith, G., Byriel, K. A., Kennard, C. H. L., Whittaker, A. K. (1994). *Aust. J. Chem.* **47**, 309–319.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Smith, G., Gentner, J. M., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Aust. J. Chem.* **48**, 1151–1161.
- Spek, A. L. (1990). *Acta Cryst.* A46, C-34.
- Takusagawa, F. & Shimada, A. (1973). *Chem. Lett.* pp. 1121–1122.
- Voogd, J., Verzijl, B. H. M. & Duisenberg, A. J. M. (1980). *Acta Cryst.* B36, 2805–2806.

*Acta Cryst.* (1995). C51, 2633–2637

## Novel Six- and Eight-Membered Heterocycles. A Trithiadiazaphosphorinane and a Pentathiadiazaphosphocine

STEVEN E. BOTTLE, RAYMOND C. BOTT, GRAHAM SMITH AND URS D. WERMUTH

*School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane 4001, Australia*

COLIN H. L. KENNARD

*Department of Chemistry, The University of Queensland, Brisbane 4072, Australia*

(Received 24 March 1995; accepted 6 July 1995)

## Abstract

We report the single-crystal X-ray structure determinations of two novel phosphorus-, nitrogen- and sulfur-containing heterocycles, namely, 4,6-bis[2-(2-methyl)propyl]-5-oxo-5-phenyl-1,2,3,4,6,5-trithiadiazaphosphorinane,  $C_{14}H_{23}N_2OPS_3$ , and 6,8-bis[2-(2-methyl)propyl]-7-oxo-7-phenyl-1,2,3,4,5,6,8,7-pentathiadiazaphosphocine,  $C_{14}H_{23}N_2OPS_5$ . The phosphorinane compound is