

| | | | | |
|-----|-------------|-------------|--------------|-------------|
| C1 | 0.0829 (2) | 0.4325 (2) | 0.30851 (11) | 0.0428 (5) |
| C2 | 0.2063 (2) | 0.3707 (2) | 0.33265 (11) | 0.0445 (5) |
| C3 | 0.2916 (2) | 0.4784 (2) | 0.33683 (12) | 0.0526 (5) |
| C4 | 0.4344 (3) | 0.4912 (4) | 0.3584 (3) | 0.0853 (10) |
| C5 | 0.2378 (2) | 0.2258 (2) | 0.35330 (12) | 0.0500 (5) |
| C6 | 0.1431 (3) | 0.0036 (3) | 0.3708 (2) | 0.0839 (9) |
| C7 | 0.0101 (5) | -0.0499 (5) | 0.3702 (5) | 0.152 (3) |
| C8 | -0.0474 (2) | 0.3649 (2) | 0.29457 (11) | 0.0435 (5) |
| C9 | -0.0960 (2) | 0.3308 (2) | 0.21868 (12) | 0.0468 (5) |
| C10 | -0.0335 (2) | 0.3707 (2) | 0.15184 (13) | 0.0566 (6) |
| C11 | -0.0842 (3) | 0.3325 (3) | 0.08003 (15) | 0.0679 (7) |
| C12 | -0.1978 (3) | 0.2492 (3) | 0.0703 (2) | 0.0750 (8) |
| C13 | -0.2604 (3) | 0.2103 (3) | 0.1314 (2) | 0.0693 (7) |
| C14 | -0.2149 (2) | 0.2515 (2) | 0.20774 (13) | 0.0537 (6) |
| C15 | -0.2826 (2) | 0.2179 (2) | 0.27087 (14) | 0.0586 (6) |
| C16 | -0.2382 (2) | 0.2572 (2) | 0.34538 (13) | 0.0510 (5) |
| C17 | -0.3089 (2) | 0.2259 (3) | 0.4109 (2) | 0.0638 (7) |
| C18 | -0.2626 (2) | 0.2627 (3) | 0.4829 (2) | 0.0683 (7) |
| C19 | -0.1416 (2) | 0.3325 (3) | 0.49531 (15) | 0.0632 (6) |
| C20 | -0.0712 (2) | 0.3641 (2) | 0.43541 (12) | 0.0527 (5) |
| C21 | -0.1166 (2) | 0.3299 (2) | 0.35788 (12) | 0.0457 (5) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|------------|--------------|------------|
| O1—N1 | 1.421 (2) | C1—C8 | 1.489 (3) |
| O2—C5 | 1.199 (2) | C2—C5 | 1.469 (3) |
| O3—C5 | 1.327 (2) | C3—C4 | 1.487 (3) |
| O3—C6 | 1.451 (3) | C6—C7 | 1.459 (5) |
| N1—C1 | 1.306 (3) | | |
| C5—O3—C6 | 117.8 (2) | O3—C5—C2 | 110.8 (2) |
| C2—C1—C8 | 128.9 (2) | O3—C6—C7 | 106.5 (3) |
| C3—C2—C5 | 125.8 (2) | C21—C8—C1 | 119.1 (2) |
| C1—C2—C5 | 129.6 (2) | C9—C8—C1 | 119.7 (2) |
| O2—C5—C2 | 125.0 (2) | | |
| C6—O3—C5—O2 | 5.5 (4) | C5—O3—C6—C7 | 167.7 (4) |
| C6—O3—C5—C2 | -172.9 (2) | N1—C1—C8—C21 | -101.2 (2) |
| C3—C2—C5—O2 | 0.1 (3) | C2—C1—C8—C21 | 78.2 (3) |
| C1—C2—C5—O2 | -176.1 (2) | N1—C1—C8—C9 | 82.1 (2) |
| C3—C2—C5—O3 | 178.6 (2) | C2—C1—C8—C9 | -98.5 (2) |
| C1—C2—C5—O3 | 2.4 (3) | | |

The raw data file obtained from the reflection frames contains directional cosines and was used as the ψ -data file for the absorption correction. The measured intensities were corrected for Lorentz and polarization effects.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993a). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1993b). Software used to prepare material for publication: *SHELXTL-Plus*.

The single crystal CCD X-ray facility at the University of Idaho was established with the assistance of NSF-EPSCoR program under NSF OSR-9350539 and the M. J. Murdock Charitable Trust, Vancouver, WA.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1222). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bialer, M., Yagen, B. & Mechoulam, R. (1978). *Tetrahedron*, **34**, 2389–2391.
- Campana, C. F., Shepard, D. F. & Litchman, W. M. (1980). *Inorg. Chem.* **20**, 4039–4044.
- McKenna, J. I., Schlicksupp, L., Natale, N. R., Willett, R. D., Maryanoff, B. E. & Flaim, S. F. (1988). *J. Med. Chem.* **31**, 473–476.
- Mosher, M. D. & Natale, N. R. (1995a). *J. Heterocycl. Chem.* **32**, 779–781.
- Mosher, M. D. & Natale, N. R. (1995b). *J. Heterocycl. Chem.* **32**, 1385–1387.
- Niou, C. S. & Natale, N. R. (1986). *Heterocycles*, **24**, 401–412.
- Nishiwaki, E., Lee, H., Matsumoto, T., Toyooka, K., Sakurai, H. & Shibuya, M. (1990). *Tetrahedron Lett.* **31**, 1299–1302.
- Schauer, C. K., Anderson, O. P., Natale, N. R. & Quincy, D. A. (1986). *Acta Cryst.* **C42**, 884–886.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993a). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993b). *SHELXTL-Plus*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART and SAINT Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Smith, M. P., Mirzaei, Y. R., Natale, N. R., Scott, B. & Willett, R. D. (1991). *Acta Cryst.* **C47**, 1328–1330.
- Turchin, K. F., Grokhovskii, S. L., Zhuze, A. L. & Gottikh, B. P. (1978). *Bioorg. Khim.* **4**, 1065–1077.
- Verner, E. J., Oliver, B. J., Schlicksupp, L. & Natale, N. R. (1990). *Heterocycles*, **31**, 327–339.

Acta Cryst. (1996). **C52**, 2515–2520

Monospiroaryloxyphosphazenes: *p*-Fluorophenoxy Derivatives Containing the 1,2-Phenylenedioxy and 2,3-Naphthalenedioxy Groups

ASHWANI VIJ, RICHARD J. STAPLES, ROBERT L. KIRCHMEIER AND JEAN'NE M. SHREEVE*

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA. E-mail: jshreeve@uidaho.edu

(Received 15 February 1996; accepted 7 May 1996)

Abstract

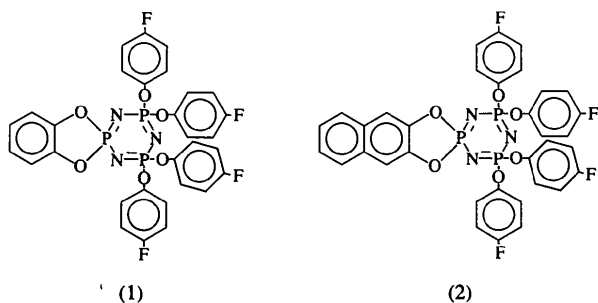
The reactions of *p*-FC₆H₄OSiMe₃ with N₃P₃F₄X [where X is either 1,2-O₂C₆H₄ or 2,3-O₂C₁₀H₆] provide a convenient route to fully substituted phosphazenes, N₃P₃(*p*-FC₆H₄O)₄X. The X-ray structures of the monospiro phosphazene derivatives of 1,2-benzenediol [4,4,6,6-tetrakis(4-fluorophenoxy)-2,2-(1,2-phenylenedioxy)-1,3,5,2,4,6-cyclophosphazene, (1), C₃₀H₂₀F₄N₃O₆P₃] and 2,3-naphthalenediol [4,4,6,6-tetrakis(4-fluorophenoxy)-2,2-(1,2-naphthalenedioxy)-1,3,5,2,4,6-cyclophosphazene, (2), C₃₄H₂₂F₄N₃O₆P₃] contain an almost planar N₃P₃ core which lies perpendicular to the planar five-membered spiro group. The F atoms of the phenoxy groups are involved in the for-

mation of weak intermolecular hydrogen bonds giving rise to dimeric networks in (1) and three-dimensional networks in (2).

Comment

A large number of structural investigations has been carried out on cyclic phosphazenes containing an aromatic spirocyclic substituent (Chandrasekhar, Murlidhara & Selvraj, 1990). All of the structures that involve the 1,2-benzenediol and 2,3-naphthalenediol groups contain only a trispirophosphazene moiety. These compounds are known to form channel-type clathrates with a variety of guest molecules, namely aromatic and aliphatic hydrocarbons, halocarbons, nitriles, esters, ketones, water, CS₂, *etc.* (Allcock, 1984). The structures of tris(1,2-phenylenedioxy)cyclotriphosphazene (TPDOCTP) with benzene, *o*- and *p*-xylene, mesitylene (Allcock, 1984) and water (Allcock, Levine & Whittle, 1986), and of tris(2,3-naphthalenedioxy)cyclotriphosphazene (TNDOCTP) with benzene (Allcock & Stein, 1974), *p*-xylene (Kubono, Asaka, Isoda, Kobayashi & Taga, 1993) and *p*-chlorotoluene (Kubono, Asaka, Taga, Isoda & Kobayashi, 1994) have been reported. Recently, the X-ray structures of guest-free TPDOCTP (Allcock, Levine & Whittle, 1986) and TNDOCTP (Kubono, Asaka, Isoda, Kobayashi & Taga, 1994) have been elucidated.

The synthesis of monospiro 1,2-phenylenedioxy-cyclophosphazene has been problematic owing to degradation of the reaction products (Allcock & Kugel, 1966). A synthetic methodology involving 1,2-bis-(trimethylsilyl)benzenediol and excess N₃P₃F₆ affords the first examples of structurally characterized fluorocyclophosphazenes, *i.e.* monospiro N₃P₃F₄(1,2-O₂C₆H₄) (3), dispiro N₃P₃F₂(1,2-O₂C₆H₄)₂ (4) and monospiro N₃P₃F₄(2,3-O₂C₁₀H₆) (5) (Vij, Geib, Kirchmeier & Shreeve, 1996). We present here the structure determinations of 4,4,6,6-tetrakis(4-fluorophenoxy)-2,2-(1,2-phenylenedioxy)-1,3,5,2,4,6-cyclophosphazene, (1), and 4,4,6,6-tetrakis(4-fluorophenoxy)-2,2-(1,2-naphthalenedioxy)-1,3,5,2,4,6-cyclophosphazene, (2).



The displacement ellipsoid plot with the atomic numbering scheme for (1) is shown in Fig. 1. Analysis of the structural data shows that unlike in the parent

compound (3), the N₃P₃ core is distorted from perfect planarity. The N1 and P1 atoms show maximum deviations of $-0.055(1)$ and $0.060(1)$ Å, respectively, from the r.m.s. deviation of 0.041 Å for the N₃P₃ core; this is greater than that found in compound (4) [r.m.s. deviation 0.0145 , N1 0.0208 and P1 0.0294 Å]. The remaining atoms in compound (1), N2, P2, N3 and P3, deviate by $0.042(1)$, $0.003(1)$, $-0.015(1)$ and $-0.036(1)$ Å, respectively. The five-membered spirocyclic PO₂C₂ ring lies roughly perpendicular to the N₃P₃ ring [$88.6(1)^\circ$] and is slightly bent at the O atoms as is evident from the torsion angle values of $3.0(3)^\circ$ for P1—O1—C1—C2 and $-4.6(3)^\circ$ for P1—O2—C2—C1. Compound (3) belongs to the *Imma* space group, with atoms P1 and N1 lying at the intersection of two mirror planes which results in a planar PO₂C₂ ring. The distortion of the 1,2-phenylenedioxy groups at the O atoms appears to be a function of the number of spirocyclic groups on the N₃P₃ ring. In compound (4), which contains two spiro groups, the PO₂C₂ rings show greater P—O—C—C torsion-angle values of $4.1(4)$ and $-5.9(4)^\circ$ at P1, and $5.9(5)$ and $-6.5(5)^\circ$ at P2, whereas in trispiro N₃P₃(1,2-O₂C₆H₄)₃ (Allcock, Levine & Whittle, 1986), the average values are even greater at ~ 7 , ~ 14 and $\sim 15^\circ$.

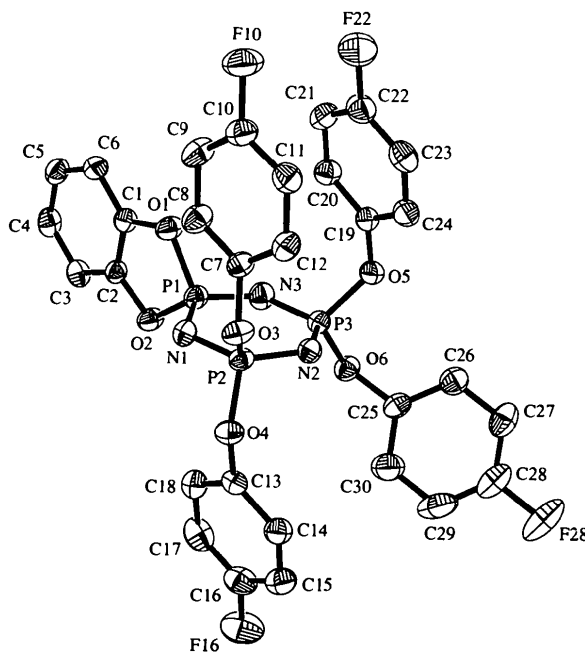


Fig. 1. The molecular structure of compound (1) showing the labeling scheme and 50% probability displacement ellipsoids.

In the case of N₃P₃(*p*-FC₆H₄O)₆, the aryl rings are stacked roughly perpendicular to the N₃P₃ ring. For compound (1), the mean planes of the fluoroaryloxy and N₃P₃ rings make dihedral angles of $90.0(1)$ for C7—C12 and $101.5(1)^\circ$ for C13—C18 (bonded to P2),

and $104.3(1)^\circ$ for C19–C24 and $63.0(1)^\circ$ for C25–C30 (bonded to P3). These values are greater than those found in $N_3P_3(2,2'-O_2C_{12}H_8)(p-FC_6H_4)_4$ (Vij, Geib, Kirchmeier & Shreeve, 1996) owing to the presence of the less sterically demanding (*vis-à-vis* 2,2'-biphenoxy) 1,2-phenylenedioxy group. The conformations of the fluoroaryloxy rings on P2 and P3 are seen from the torsion angles C7–O3–P2–O4 $-175.1(2)$, C13–O4–P2–O3 $-172.2(2)$, C19–O5–P3–O6 $-177.5(2)$ and C25–O6–P3–O5 $70.0(2)^\circ$. This difference in stacking behavior results in a mean-plane angle between rings C7–C12 and C13–C18 of $11.7(1)^\circ$ versus a mean-plane angle between rings C19–C24 and C25–C30 of $52.1(1)^\circ$. The packing diagram of (1) (Fig. 2) shows the longest intermolecular contact, $H3 \cdots F28^i$ [symmetry code: (i) $1-x, 1-y, 1-z$] of $2.64(3) \text{ \AA}$, resulting in dimer formation.

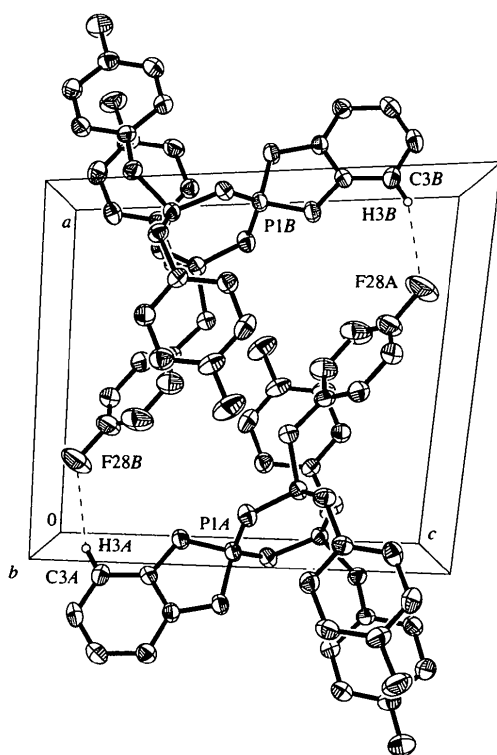


Fig. 2. Drawing of the packing of (1) showing the $H \cdots F$ interactions within the cell.

The molecular structure of compound (2) is shown in Fig. 3. Replacement of the 1,2-phenylenedioxy group in (1) with the 2,3-naphthalenedioxy group results in a lower distortion of the N_3P_3 ring. The maximum deviation occurs for the N1 and P2 atoms, with values of $-0.019(1)$ and $0.023(1) \text{ \AA}$, respectively. The r.m.s. deviation of the N_3P_3 ring (0.014 \AA) is less than that found in both compound (5) (0.0353 \AA) and guest-free TNDCTP (Kubono, Asaka, Isoda, Kobayashi & Taga,

1994). The naphthalene group is approximately planar [maximum deviation for atom C6 is $0.010(3) \text{ \AA}$] and lies nearly perpendicular to the N_3P_3 group [$89.2(1)^\circ$]. The five-membered spirocycle is slightly bent at the O atoms, as seen from the torsion angles P1–O1–C2–C3 $-1.9(3)$ and P1–O2–C3–C2 $1.4(3)^\circ$. As a consequence, there is some diversity in the C–C bond

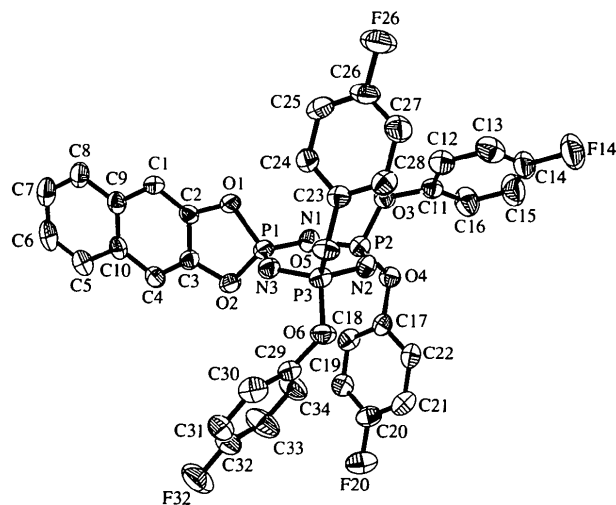


Fig. 3. The molecular structure of compound (2) showing the labeling scheme and 50% probability displacement ellipsoids.

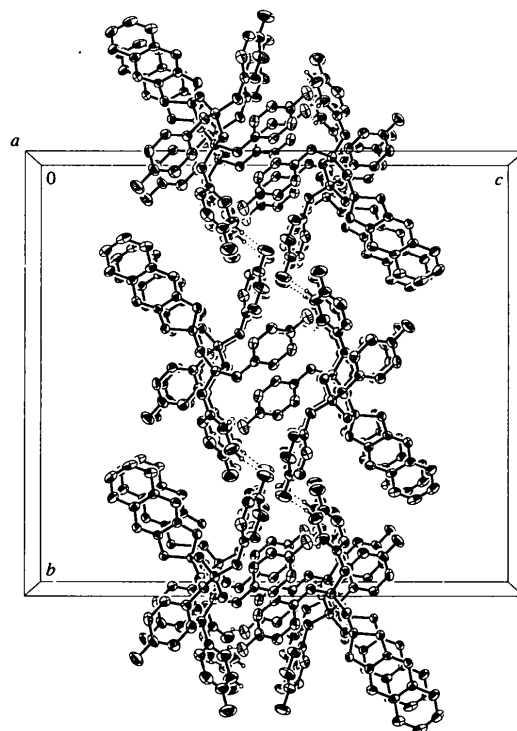


Fig. 4. Drawing of the packing of (2) showing the $H \cdots F$ interactions within the cell.

lengths in the naphthalene ring, *i.e.* C1—C2 1.346 (4) and C1—C9 1.429 (4) Å. Both the magnitude of ring bending and the bond-length diversity, however, are lower than in TNDCTP, where the torsion angles vary from 8.4 (6) to 18.6 (6)° and the naphthalene bond lengths vary from 1.320 (8) to 1.448 (9) Å (Kubono, Asaka, Isoda, Kobayashi & Taga, 1994). The *p*-fluorophenoxy rings are stacked in a more ordered manner compared with compound (1), and the relative dihedral angles between the mean planes of the N₃P₃ ring and the aryl groups are 47.5 (1) for C11—C16 and 106.6 (1)° for C17—C22 (bonded to P2), and 108.3 (1) for C23—C28 and 58.6 (1)° for C29—C34 (bonded to P3). The *p*-fluoroaryloxy rings are twisted with respect to one another, with an angle of 74.9 (1)° for those on atom P2 and 94.0 (1)° for those on atom P3. Two long-range intermolecular interactions, *i.e.* H15ⁱⁱ ··· F32ⁱⁱ of 2.39 (5) and H16ⁱⁱⁱ ··· F20ⁱⁱⁱ of 2.46 (4) Å [symmetry codes: (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, z$; (iii) $2 - x, -y, 1 - z$], are observed in the crystal packing of compound (2) leading to a three-dimensional network (Fig. 4).

Absorption correction:
semi-empirical (Siemens,
1995a)
 $T_{\min} = 0.8434$, $T_{\max} =$
0.9803
8172 measured reflections
5588 independent reflections
4645 observed reflections
 $[I > 2\sigma(I)]$

$h = -14 \rightarrow 9$
 $k = -16 \rightarrow 11$
 $l = -15 \rightarrow 16$
Crystal decay from 50
frames of reflection
data monitored at the
start and end of data
collection
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.0454$
 $wR(F^2) = 0.1157$
 $S = 1.037$
5587 reflections
496 parameters
H atoms obtained from
difference map and all
parameters refined, C—H
0.90 (3)—0.99 (3) Å
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2$
 $+ 1.3332P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
 $\Delta\rho_{\max} = 0.254 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.338 \text{ e } \text{Å}^{-3}$
Extinction correction:
SHELXL93 (Sheldrick,
1993)
Extinction coefficient:
0.0067 (8)
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Experimental

Compounds (1) and (2) were prepared by the reaction of N₃P₃F₄X₂ (X = 1,2-O₂C₆H₄ and 2,3-O₂C₁₀H₆, respectively) with a slight excess of *p*-FC₆H₄OSiMe₃ in tetrahydrofuran at ~353 K using CsF as catalyst. Removal of the solvent and excess siloxane at ~373 K/0.03 Torr overnight, followed by extraction in chloroform and recrystallization from a chloroform/cyclohexane mixture afforded the desired products. The EI/MS analyses of compounds (1) and (2) show the M^+ peaks as the highest peaks with *m/e* values of 687 and 737, with intensities of 41 and 47%, respectively. The base peak corresponds to the $(M-\text{OC}_6\text{H}_4\text{F})^+$ fragment. The multinuclear NMR spectral data are described elsewhere (Vij, Geib, Kirchmeier & Shreeve, 1996).

Compound (1)

Crystal data

C₃₀H₂₀F₄N₃O₆P₃

$M_r = 687.40$

Triclinic

$P\bar{1}$

$a = 11.3869 (3) \text{ Å}$

$b = 12.6938 (4) \text{ Å}$

$c = 12.8468 (4) \text{ Å}$

$\alpha = 62.040 (1)^\circ$

$\beta = 74.175 (1)^\circ$

$\gamma = 63.795 (1)^\circ$

$V = 1466.53 (8) \text{ Å}^3$

$Z = 2$

$D_x = 1.557 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ Å}$

Cell parameters from 131
reflections

$\theta = 1.8\text{--}27.53^\circ$

$\mu = 0.279 \text{ mm}^{-1}$

$T = 203 (2) \text{ K}$

Block

$0.35 \times 0.20 \times 0.15 \text{ mm}$

Colorless

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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_{eq} |
|-----|-------------|-------------|--------------|-----------------|
| P1 | 0.01642 (6) | 0.72563 (6) | 0.50207 (5) | 0.0290 (2) |
| P2 | 0.05103 (6) | 0.51369 (6) | 0.71788 (5) | 0.0266 (2) |
| P3 | 0.18942 (6) | 0.67331 (6) | 0.64997 (6) | 0.0283 (2) |
| F10 | -0.4912 (2) | 0.8531 (2) | 0.9499 (2) | 0.0542 (5) |
| F16 | 0.5815 (2) | 0.1253 (2) | 0.5353 (2) | 0.0673 (6) |
| F22 | -0.3020 (2) | 0.9950 (2) | 0.9119 (2) | 0.0621 (5) |
| F28 | 0.7379 (2) | 0.3040 (2) | 0.9135 (2) | 0.0882 (8) |
| O1 | -0.1230 (2) | 0.8461 (2) | 0.48146 (15) | 0.0351 (4) |
| O2 | 0.0471 (2) | 0.7337 (2) | 0.36878 (15) | 0.0343 (4) |
| O3 | -0.0619 (2) | 0.4958 (2) | 0.8213 (2) | 0.0332 (4) |
| O4 | 0.1156 (2) | 0.3660 (2) | 0.74237 (15) | 0.0309 (4) |
| O5 | 0.1748 (2) | 0.7627 (2) | 0.7111 (2) | 0.0328 (4) |
| O6 | 0.3425 (2) | 0.6286 (2) | 0.6145 (2) | 0.0335 (4) |
| N1 | -0.0074 (2) | 0.5982 (2) | 0.5920 (2) | 0.0311 (5) |
| N2 | 0.1469 (2) | 0.5567 (2) | 0.7441 (2) | 0.0287 (5) |
| N3 | 0.1211 (2) | 0.7571 (2) | 0.5293 (2) | 0.0346 (5) |
| C1 | -0.1462 (2) | 0.9057 (2) | 0.3618 (2) | 0.0284 (5) |
| C2 | -0.0486 (2) | 0.8423 (2) | 0.2975 (2) | 0.0277 (5) |
| C3 | -0.0484 (3) | 0.8861 (3) | 0.1769 (2) | 0.0334 (6) |
| C4 | -0.1546 (3) | 0.9970 (3) | 0.1239 (2) | 0.0371 (6) |
| C5 | -0.2535 (3) | 1.0592 (3) | 0.1892 (2) | 0.0369 (6) |
| C6 | -0.2521 (3) | 1.0144 (2) | 0.3112 (2) | 0.0324 (6) |
| C7 | -0.1680 (2) | 0.5949 (2) | 0.8477 (2) | 0.0287 (5) |
| C8 | -0.2518 (3) | 0.6977 (3) | 0.7636 (2) | 0.0368 (6) |
| C9 | -0.3610 (3) | 0.7858 (3) | 0.7984 (3) | 0.0410 (7) |
| C10 | -0.3836 (3) | 0.7671 (3) | 0.9150 (3) | 0.0363 (6) |
| C11 | -0.3013 (3) | 0.6650 (3) | 0.9998 (3) | 0.0372 (6) |
| C12 | -0.1910 (3) | 0.5785 (3) | 0.9649 (2) | 0.0333 (6) |
| C13 | 0.2369 (2) | 0.3122 (2) | 0.6854 (2) | 0.0282 (5) |
| C14 | 0.3362 (3) | 0.2152 (3) | 0.7564 (2) | 0.0343 (6) |
| C15 | 0.4538 (3) | 0.1526 (3) | 0.7057 (3) | 0.0409 (7) |
| C16 | 0.4670 (3) | 0.1890 (3) | 0.5857 (3) | 0.0436 (7) |
| C17 | 0.3694 (3) | 0.2858 (3) | 0.5134 (3) | 0.0442 (7) |
| C18 | 0.2508 (3) | 0.3492 (3) | 0.5636 (2) | 0.0348 (6) |
| C19 | 0.0510 (2) | 0.8212 (2) | 0.7618 (2) | 0.0297 (5) |
| C20 | -0.0438 (3) | 0.9259 (3) | 0.6894 (2) | 0.0341 (6) |
| C21 | -0.1640 (3) | 0.9859 (3) | 0.7403 (3) | 0.0408 (7) |
| C22 | -0.1839 (3) | 0.9373 (3) | 0.8615 (3) | 0.0403 (7) |
| C23 | -0.0904 (3) | 0.8344 (3) | 0.9345 (3) | 0.0407 (7) |
| C24 | 0.0298 (3) | 0.7758 (3) | 0.8835 (2) | 0.0357 (6) |

Data collection

Siemens CCD diffractometer

$R_{\text{int}} = 0.0249$

ω scans

$\theta_{\text{max}} = 27.53^\circ$

| | | | | |
|-----|------------|------------|------------|-------------|
| C25 | 0.4389 (2) | 0.5440 (2) | 0.6966 (2) | 0.0326 (6) |
| C26 | 0.4583 (3) | 0.5816 (3) | 0.7738 (3) | 0.0390 (6) |
| C27 | 0.5604 (3) | 0.4993 (3) | 0.8473 (3) | 0.0481 (8) |
| C28 | 0.6379 (3) | 0.3846 (3) | 0.8403 (3) | 0.0554 (9) |
| C29 | 0.6205 (4) | 0.3460 (3) | 0.7644 (4) | 0.0638 (10) |
| C30 | 0.5185 (3) | 0.4276 (3) | 0.6905 (3) | 0.0507 (8) |

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

| | | | |
|----------|-------------|-----------|-------------|
| P1—N3 | 1.576 (2) | F22—C22 | 1.365 (3) |
| P1—N1 | 1.577 (2) | F28—C28 | 1.371 (3) |
| P1—O2 | 1.614 (2) | O1—C1 | 1.400 (3) |
| P1—O1 | 1.623 (2) | O2—C2 | 1.400 (3) |
| P2—N2 | 1.582 (2) | O3—C7 | 1.411 (3) |
| P2—O4 | 1.584 (2) | O4—C13 | 1.412 (3) |
| P2—O3 | 1.585 (2) | O5—C19 | 1.412 (3) |
| P2—N1 | 1.593 (2) | O6—C25 | 1.414 (3) |
| P3—O6 | 1.582 (2) | C1—C6 | 1.377 (3) |
| P3—N3 | 1.588 (2) | C1—C2 | 1.379 (3) |
| P3—N2 | 1.588 (2) | C2—C3 | 1.378 (3) |
| P3—O5 | 1.591 (2) | C3—C4 | 1.398 (4) |
| F10—C10 | 1.368 (3) | C4—C5 | 1.385 (4) |
| F16—C16 | 1.368 (3) | C5—C6 | 1.397 (4) |
| N3—P1—N1 | 117.91 (11) | N3—P3—N2 | 117.53 (11) |
| N3—P1—O2 | 109.61 (11) | O6—P3—O5 | 99.94 (10) |
| N1—P1—O2 | 110.93 (11) | N3—P3—O5 | 110.35 (11) |
| N3—P1—O1 | 110.30 (11) | N2—P3—O5 | 109.51 (10) |
| N1—P1—O1 | 109.35 (11) | C1—O1—P1 | 109.65 (15) |
| O2—P1—O1 | 96.68 (9) | C2—O2—P1 | 109.72 (15) |
| N2—P2—O4 | 110.94 (10) | C7—O3—P2 | 126.0 (2) |
| N2—P2—O3 | 111.51 (11) | C13—O4—P2 | 122.9 (2) |
| O4—P2—O3 | 93.54 (9) | C19—O5—P3 | 119.80 (15) |
| N2—P2—N1 | 116.26 (11) | C25—O6—P3 | 124.1 (2) |
| O4—P2—N1 | 111.19 (10) | P1—N1—P2 | 122.76 (13) |
| O3—P2—N1 | 111.16 (10) | P2—N2—P3 | 122.97 (13) |
| O6—P3—N3 | 106.03 (11) | P1—N3—P3 | 121.73 (14) |
| O6—P3—N2 | 112.04 (10) | | |

Compound (2)

Crystal data

 $\text{C}_{34}\text{H}_{22}\text{F}_4\text{N}_3\text{O}_6\text{P}_3$ $M_r = 737.46$

Orthorhombic

Pbca

 $a = 8.1325 (1) \text{\AA}$ $b = 26.5942 (3) \text{\AA}$ $c = 29.8727 (5) \text{\AA}$ $V = 6460.8 (2) \text{\AA}^3$ $Z = 8$ $D_x = 1.516 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Siemens CCD diffractometer
 ω scans

Absorption correction:

semi-empirical (Siemens,
1995a) $T_{\min} = 0.8597$, $T_{\max} =$
0.9757

23340 measured reflections

4602 independent reflections

3449 observed reflections

 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2 $R(F) = 0.0468$ $wR(F^2) = 0.1125$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{\AA}$ Cell parameters from 214
reflections $\theta = 1.53\text{--}23.23^\circ$ $\mu = 0.259 \text{ mm}^{-1}$ $T = 203 (2) \text{ K}$

Plate

 $0.20 \times 0.15 \times 0.15 \text{ mm}$

Colorless

 $R_{\text{int}} = 0.0593$ $\theta_{\text{max}} = 23.23^\circ$ $h = -9 \rightarrow 8$ $k = -24 \rightarrow 29$ $l = -32 \rightarrow 33$

Crystal decay from 50

frames of reflection

data monitored at the

start and end of data

collection

intensity decay: none

 $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.220 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.286 \text{ e \AA}^{-3}$ $S = 1.085$

4601 reflections

540 parameters

H atoms obtained from
difference map and all
parameters refined, C—H
0.83 (3)—0.97 (4) \AA $w = 1/[\sigma^2(F_o^2) + (0.0283P)^2$
 $+ 5.2062P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:

SHELXL93 (Sheldrick,
1993)

Extinction coefficient:

0.00093 (10)

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992,Vol. C, Tables 4.2.6.8 and
6.1.1.4)Table 3. Fractional atomic coordinates and equivalent
isotropic displacement parameters (\AA^2) for (2)

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

| | x | y | z | U_{eq} |
|-----|--------------|---------------|--------------|-----------------|
| P1 | 0.68951 (11) | 0.09392 (3) | 0.66268 (3) | 0.0355 (2) |
| P2 | 0.70453 (10) | 0.00391 (3) | 0.61651 (3) | 0.0348 (2) |
| P3 | 0.41897 (10) | 0.06074 (3) | 0.61425 (3) | 0.0340 (2) |
| F14 | 0.4853 (4) | -0.22961 (8) | 0.58888 (9) | 0.0975 (9) |
| F20 | 0.8657 (2) | 0.12434 (8) | 0.43545 (6) | 0.0624 (6) |
| F26 | 0.1733 (3) | -0.10325 (8) | 0.76060 (7) | 0.0746 (7) |
| F32 | 0.5403 (3) | 0.27617 (7) | 0.51783 (8) | 0.0829 (8) |
| O1 | 0.6931 (3) | 0.09828 (7) | 0.71649 (6) | 0.0374 (5) |
| O2 | 0.7954 (3) | 0.14391 (8) | 0.65252 (7) | 0.0414 (6) |
| O3 | 0.7214 (3) | -0.04681 (8) | 0.64346 (7) | 0.0396 (6) |
| O4 | 0.8192 (2) | -0.00898 (7) | 0.57479 (7) | 0.0370 (5) |
| O5 | 0.2466 (2) | 0.04397 (8) | 0.63386 (7) | 0.0378 (5) |
| O6 | 0.3454 (3) | 0.08869 (8) | 0.57181 (7) | 0.0412 (6) |
| N1 | 0.7859 (3) | 0.04614 (9) | 0.64668 (8) | 0.0378 (7) |
| N2 | 0.5224 (3) | 0.01311 (9) | 0.59959 (8) | 0.0336 (6) |
| N3 | 0.5071 (3) | 0.10015 (9) | 0.64569 (8) | 0.0358 (7) |
| C1 | 0.7975 (4) | 0.15804 (12) | 0.77200 (11) | 0.0363 (8) |
| C2 | 0.7756 (4) | 0.14206 (11) | 0.72967 (10) | 0.0320 (8) |
| C3 | 0.8354 (4) | 0.16847 (12) | 0.69267 (10) | 0.0352 (8) |
| C4 | 0.9207 (4) | 0.21205 (12) | 0.69680 (12) | 0.0395 (9) |
| C5 | 1.0356 (5) | 0.27588 (13) | 0.7486 (2) | 0.0503 (10) |
| C6 | 1.0607 (5) | 0.2931 (2) | 0.7909 (2) | 0.0578 (11) |
| C7 | 0.9981 (5) | 0.26717 (15) | 0.8276 (2) | 0.0569 (11) |
| C8 | 0.9133 (5) | 0.22351 (14) | 0.82169 (13) | 0.0473 (10) |
| C9 | 0.8853 (4) | 0.20403 (12) | 0.77840 (11) | 0.0376 (8) |
| C10 | 0.9470 (4) | 0.23048 (11) | 0.74083 (11) | 0.0378 (8) |
| C11 | 0.6575 (4) | -0.09300 (12) | 0.62758 (10) | 0.0361 (8) |
| C12 | 0.5105 (5) | -0.10931 (14) | 0.64404 (13) | 0.0469 (10) |
| C13 | 0.4514 (5) | -0.1557 (2) | 0.63052 (15) | 0.0581 (11) |
| C14 | 0.5429 (6) | -0.18336 (14) | 0.60122 (14) | 0.0611 (12) |
| C15 | 0.6886 (7) | -0.1677 (2) | 0.5851 (2) | 0.0724 (13) |
| C16 | 0.7466 (6) | -0.12135 (15) | 0.59832 (14) | 0.0611 (11) |
| C17 | 0.8314 (4) | 0.02547 (12) | 0.53918 (10) | 0.0345 (8) |
| C18 | 0.9433 (4) | 0.06434 (13) | 0.54166 (12) | 0.0407 (9) |
| C19 | 0.9559 (4) | 0.09729 (14) | 0.50609 (12) | 0.0429 (9) |
| C20 | 0.8559 (4) | 0.09081 (13) | 0.46992 (11) | 0.0434 (9) |
| C21 | 0.7458 (4) | 0.05201 (14) | 0.46676 (12) | 0.0453 (9) |
| C22 | 0.7333 (4) | 0.01881 (14) | 0.50197 (11) | 0.0409 (9) |
| C23 | 0.2335 (4) | 0.00610 (12) | 0.66690 (10) | 0.0349 (8) |
| C24 | 0.3034 (4) | 0.01212 (13) | 0.70839 (11) | 0.0403 (9) |
| C25 | 0.2836 (5) | -0.02502 (14) | 0.74041 (12) | 0.0471 (9) |
| C26 | 0.1928 (4) | -0.06645 (13) | 0.72928 (12) | 0.0472 (9) |
| C27 | 0.1204 (5) | -0.07262 (15) | 0.68845 (13) | 0.0492 (10) |
| C28 | 0.1410 (4) | -0.03563 (13) | 0.65648 (12) | 0.0411 (9) |
| C29 | 0.3986 (4) | 0.13696 (12) | 0.55889 (10) | 0.0352 (8) |
| C30 | 0.2937 (5) | 0.17652 (14) | 0.56415 (12) | 0.0478 (10) |
| C31 | 0.3438 (6) | 0.22389 (15) | 0.55030 (13) | 0.0546 (11) |
| C32 | 0.4944 (5) | 0.22904 (13) | 0.53198 (13) | 0.0534 (10) |
| C33 | 0.6012 (6) | 0.1905 (2) | 0.5271 (2) | 0.0683 (13) |
| C34 | 0.5506 (5) | 0.1434 (2) | 0.54093 (14) | 0.0566 (11) |

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

| | | | |
|-------|-----------|--------|-----------|
| P1—N1 | 1.567 (3) | O2—C3 | 1.404 (3) |
| P1—N3 | 1.576 (3) | O3—C11 | 1.415 (4) |
| P1—O1 | 1.612 (2) | O4—C17 | 1.407 (4) |
| P1—O2 | 1.613 (2) | O5—C23 | 1.414 (3) |
| P2—O3 | 1.577 (2) | O6—C29 | 1.408 (3) |

| | | | |
|----------|-------------|-----------|-------------|
| P2—N2 | 1.584 (3) | C1—C2 | 1.346 (4) |
| P2—N1 | 1.585 (3) | C1—C9 | 1.429 (4) |
| P2—O4 | 1.594 (2) | C2—C3 | 1.397 (4) |
| P3—N3 | 1.579 (3) | C3—C4 | 1.356 (4) |
| P3—N2 | 1.582 (3) | C4—C10 | 1.420 (4) |
| P3—O5 | 1.584 (2) | C5—C6 | 1.360 (5) |
| P3—O6 | 1.587 (2) | C5—C10 | 1.425 (4) |
| F14—C14 | 1.367 (4) | C6—C7 | 1.392 (6) |
| F20—C20 | 1.365 (4) | C7—C8 | 1.362 (5) |
| F26—C26 | 1.363 (3) | C8—C9 | 1.412 (5) |
| F32—C32 | 1.374 (4) | C9—C10 | 1.416 (4) |
| O1—C2 | 1.401 (3) | | |
| N1—P1—N3 | 117.22 (14) | N2—P3—O5 | 110.36 (12) |
| N1—P1—O1 | 110.70 (13) | N3—P3—O6 | 109.58 (12) |
| N3—P1—O1 | 109.30 (13) | N2—P3—O6 | 110.75 (13) |
| N1—P1—O2 | 110.12 (13) | O5—P3—O6 | 95.38 (11) |
| N3—P1—O2 | 110.80 (13) | C2—O1—P1 | 110.4 (2) |
| O1—P1—O2 | 96.82 (11) | C3—O2—P1 | 110.3 (2) |
| O3—P2—N2 | 112.11 (13) | C11—O3—P2 | 122.6 (2) |
| O3—P2—N1 | 106.24 (13) | C17—O4—P2 | 119.5 (2) |
| N2—P2—N1 | 117.53 (13) | C23—O5—P3 | 121.7 (2) |
| O3—P2—O4 | 99.46 (11) | C29—O6—P3 | 122.0 (2) |
| N2—P2—O4 | 109.33 (12) | P1—N1—P2 | 122.6 (2) |
| N1—P2—O4 | 110.66 (13) | P3—N2—P2 | 122.2 (2) |
| N3—P3—N2 | 117.02 (14) | P1—N3—P3 | 123.3 (2) |
| N3—P3—O5 | 111.64 (13) | | |

The diffraction data were collected on a Siemens three-circle diffractometer (χ axis fixed at 54.74°) equipped with a CCD detector maintained at 218.6 K, using the ω -scan technique (Campana, Shepard & Litchman, 1980). The initial cell constants were determined from reflection data obtained by collecting 60×10 s frames at a detector resolution of 512×512 pixels. The final unit-cell values, however, are based on the least-squares refinement of all the observed reflections [4645 for (1) and 3449 for (2)]. A complete hemisphere of data was scanned on ω (0.3°), with a run time of 10 s frames for a total of 1271 frames collected in three sets plus a final set of 50 frames using the *SMART Software* (Siemens, 1995c). The crystal decay was monitored through reflection data from 50 frames collected at the beginning and at the end of data collection. The data reduction was accomplished by processing the frames data using *SAINT Software* (Siemens, 1995a) to give the raw file corrected for Lp and decay. Since the raw file contains information about directional cosines, it was used for empirical absorption correction. The structures were solved by direct methods using *SHELXS86* (Sheldrick, 1990) in *SHELXTL-Plus* (Siemens, 1995b) and refined by full-matrix least-squares methods using *SHELXTL-Plus* and *SHELXL93* (Sheldrick, 1993). H atoms were located from difference Fourier syntheses and refined with isotropic displacement parameters. All computations were performed on a Silicon Graphics workstation.

The authors are grateful to the National Science Foundation (CHE-9003509) for support of this research. The single crystal CCD X-ray facility at the University of Idaho was established with the assistance of NSF-Idaho EPSCoR program under NSF OSR-9350539 and the M. J. Murdock Charitable Trust, Vancouver, Washington, USA.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, and torsion angles have been deposited with the IUCr (Reference: FG1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allcock, H. R. (1984). *Inclusion Compounds*, Vol. 1, edited by J. L. Atwood, J. E. D. Davies & D. D. MacNicol, pp. 351–374. London: Academic Press.
- Allcock, H. R. & Kugel, R. L. (1966). *Inorg. Chem.* **5**, 1016–1020.
- Allcock, H. R., Levine, M. L. & Whittle, R. R. (1986). *Inorg. Chem.* **25**, 41–47.
- Allcock, H. R. & Stein, M. T. (1974). *J. Am. Chem. Soc.* **96**, 49–52.
- Campana, C. F., Shepard, D. F. & Litchman, W. M. (1980). *Inorg. Chem.* **20**, 4039–4043.
- Chandrasekhar, V., Murlidhara, M. G. R. & Selvaraj, I. I. (1990). *Heterocycles*, **31**, 2231–2266, and references therein.
- Kubono, K., Asaka, N., Isoda, S., Kobayashi, T. & Taga, T. (1993). *Acta Cryst.* **C49**, 404–406.
- Kubono, K., Asaka, N., Isoda, S., Kobayashi, T. & Taga, T. (1994). *Acta Cryst.* **C50**, 324–326.
- Kubono, K., Asaka, N., Taga, T., Isoda, S. & Kobayashi, T. (1994). *J. Mater. Chem.* **4**, 291–297.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1995a). *SAINT Software*. Version 4.035. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995b). *SHELXTL-Plus*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995c). *SMART Software*. Version 4.043. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Vij, A., Geib, S., Kirchmeier, R. L. & Shreeve, J. M. (1996). *Inorg. Chem.* **35**, 2915–2929.

Acta Cryst. (1996). **C52**, 2520–2524

Multiple Hydrogen Bonds in Pyridine-2,6-dimethanol and Benzene-1,3,5-trimethanol

WILLIAM BELL,^a PAMELA I. COUPAR,^a GEORGE FERGUSON^b
AND CHRISTOPHER GLIDEWELL^{a*}

^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and ^bDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk

(Received 28 March 1996; accepted 8 May 1996)

Abstract

Pyridine-2,6-dimethanol, C₇H₉NO₂, forms a chain structure in which the molecules are linked by O—H···O hydrogen bonds into dimeric units lying across centres of inversion, these dimers being linked by O—H···N hydrogen bonds into chains around other centres of inversion. In the structure of benzene-1,3,5-trimethanol, C₉H₁₂O₃, the molecules form a continuous three-dimensional network in which each molecule is hydrogen-bonded to six others.