Acta Cryst. (1998). B**54**, 129–138

Chain, Sheet and Framework Structures in the Adducts of Phenylphosphonic Acid with 4,4′-Bipyridyl (1/1), Piperazine (2/1) and 1,4-Diazabicyclo[2.2.2]octane (2/1)

GEORGE FERGUSON,[a] CHRISTOPHER GLIDEWELL,[b]* RICHARD M. GREGSON[b] AND PAUL R. MEEHAN[a]

[a]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and* [b]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. E-mail: cg@st-andrews.ac.uk*

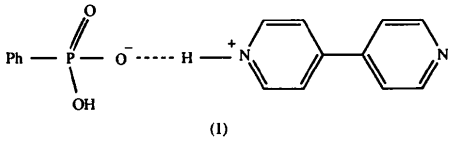
(*Received 28 April 1997; accepted 11 July 1997*)

Abstract

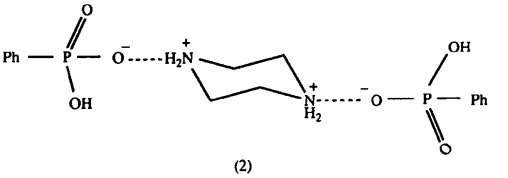
Phenylphosphonic acid–4,4′-bipyridyl (1/1), (1), $C_6H_7O_3P.C_{10}H_8N_2$, triclinic, $P\bar{1}$, a = 6.9026 (8), b = 9.7086 (9), c = 12.201 (2) Å, α = 77.138 (9), β = 74.345 (10), γ = 75.477 (8)°, with Z = 2, is a salt, $C_{10}H_9N_2^+.[C_6H_5PO_2(OH)]^-$, containing singly protonated 4,4′-bipyridyl cations: the cations and anions are linked by N—H···O and C—H···O hydrogen bonds in an $R_2^2(7)$ motif and these aggregates are linked into centrosymmetric $R_2^2(8)$ dimers by O—H···O hydrogen bonds; the dimer units are linked into chains by C—H···O hydrogen bonds. Phenylphosphonic acid–piperazine (2/1), $(C_6H_7O_3P)_2.C_4H_{10}N_2$ (2), monoclinic, $P2_1/n$, a = 6.0042 (9), b = 19.746 (3), c = 8.651 (2) Å, β = 105.63 (2)°, with Z = 2, is a salt, $C_4H_{12}N_2^{2+}.[\{C_6H_5PO_2(OH)\}^-]_2$, containing doubly protonated piperazine: the anions are linked by O—H···O hydrogen bonds into centrosymmetric $R_2^2(8)$ dimers and these dimers are linked to the centrosymmetric cations by N—H···O hydrogen bonds: each cation is hydrogen-bonded to four different anion dimers and each anion dimer is hydrogen-bonded to four different cations; the overall structure consists of two-dimensional sheets built from $R_6^4(16)$ and $R_4^4(18)$ rings. Phenylphosphonic acid–1,4-diazabicyclo[2.2.2]octane (2/1), (3), $(C_6H_7O_3P)_2.C_6H_{12}N_2$, monoclinic, $P2_1/n$, a = 6.3607 (3), b = 21.8300 (11), c = 14.5965 (9) Å, β = 92.558 (6)°, with Z = 4, is a salt in which one nitrogen of the diamine is fully protonated and the other is partially protonated: the anionic components are linked into $C(4)$ chains by O—H···O hydrogen bonds, and these chains are cross-linked *via* the diamines by means of N—H···O and O—H···N hydrogen bonds. The resulting sheets built from $R_8^8(34)$ rings are linked by C—H···O hydrogen bonds into a three-dimensional framework.

1. Introduction

In the structure of phenylphosphonic acid, $C_6H_5PO(OH)_2$, the molecules are linked together by hydrogen bonds into continuous sheets in which each molecule acts as both a double donor and a double acceptor of hydrogen bonds (Weakley, 1976). Within the sheets it is possible to identify both centrosymmetric dimers built from an $R_2^2(8)$ [P(O)OH]$_2$ motif (Etter, 1990; Bernstein *et al.*, 1995),† closely analogous to the $R_2^2(8)$ [COOH]$_2$ motif characteristic of many carboxylic acids, such as benzoic acid (Sim *et al.*, 1955; Bruno & Randaccio, 1980), and also chains built from a $C(4)$ $[\cdots O{=}P{-}O{-}H\cdots]_n$ motif, analogous to the $C(4)$ $[\cdots O{=}C{-}O{-}H\cdots]_n$ chains in acetic acid (Jones & Templeton, 1958; Nahringbauer, 1970; Jönsson, 1971). The two different types of O—H···O hydrogen bond in phenylphosphonic acid, forming rings and chains, respectively, have rather similar O···O distances and hence are probably of similar thermochemical strength: the consequent possibility that either or both of the ring and chain motifs might be retained in adducts of phenylphosphonic acid with hydrogen-bond acceptors thus makes this acid an attractive molecular tekton for crystal engineering purposes. Accordingly, we have initiated a structural study of adducts of phenylphosphonic acid with polyamines and here we report the synthesis and structures of three such adducts: a 1:1 adduct $[C_6H_5PO(OH)_2].[C_{10}H_8N_2]$ (1) formed with 4,4′-bipyridyl and two 2:1 adducts, $[C_6H_5PO(OH)_2]_2.[C_4H_{10}N_2]$ (2) and $[C_6H_5PO(OH)_2]_2.[C_6H_{12}N_2]$ (3), formed with piperazine and 1,4-diazabicyclo[2.2.2]-octane (DABCO), respectively.

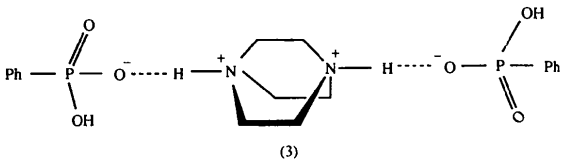


(1)



(2)

† Graph-set descriptors take the general form $G_d^a(n)$, where G can take one of four forms: S for intramolecular (self) hydrogen bonds; D for a finite dimeric system; R for a cyclic system; C for chains. The sub- and superscripts d and a define the numbers of hydrogen-bond donors and acceptors in a motif and n defines the total number of atoms in a motif. Thus, the centrosymmetric dimer [—COOH]$_2$ motif commonly found in carboxylic aids is denoted $R_2^2(8)$



(3)

2. Experimental

2.1. *Synthesis*

Samples of (1)–(3) were prepared by cocrystallization of equimolar quantities of phenylphosphonic acid with 4,4′-bipyridyl, piperazine or DABCO, respectively, from solutions in methanol. Analyses: (1) found C 61.4, H 4.8, N 8.9%; $C_{16}H_{15}N_2PO_3$ requires C 61.1, H 4.8, N 8.9%; (2) found C 47.9, H 6.0, N 7.0%; $C_{16}H_{24}N_2P_2O_6$ requires C 47.8, H 6.0, N 7.0%; (3) found C 50.2, H 6.1, N 6.6%; $C_{18}H_{26}N_2P_2O_6$ requires C 50.5, H 6.1, N 6.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. *Data collection, structure solution and refinement*

Details of cell data, data collection and refinement are summarized in Table 1. Compound (1) is triclinic; space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. For (2) and (3) the space group $P2_1/n$ was uniquely determined by systematic absences ($h0l$ absent if $h + l = 2n + 1$; $0k0$ absent if $k = 2n + 1$). The structures were solved by direct methods (Gabe *et al.*, 1989) and refined using *SHELXL*93 (Sheldrick, 1993). Absorption corrections were made using φ scans (North *et al.*, 1968) for (1) and Gaussian integration for (2) and (3). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). H atoms bonded to carbon were positioned on geometric grounds; initial coordinates for H atoms bonded to N or O were obtained from difference maps. For (3) examination of difference maps clearly showed that the H atom lying between N1 and O13 occupied a single site, adjacent to N1, but that between N2 and O23 there were, in fact, two occupied sites: one, designated H2, is adjacent to N2 and the other, designated H23, is adjacent to O23: thus, the proton transfer from O23 in one of the phenylphosphonic acid molecules to N2 of the DABCO component is incomplete. Refinement of the site-occupation factors for H2 and H23 gave values of 0.68 (4) and 0.32 (4), respectively. All the H atoms were included in the refinements as riding atoms, in geometrically idealized positions. Examination of both structures using *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the lattices. The diagrams were prepared using *ORTEP*II (Johnson, 1976), as implemented in *PLATON*, and with *PLUTON* (Spek, 1995*b*). Final fractional coordinates are presented in Table 2 and selected dimensions in Table 3.†

3. Results and discussion

3.1. *Crystal structures and hydrogen-bonding motifs*

Structure analysis of (1), (2) and (3) reveals that each is in fact a salt, with a single proton transfer from each phenylphosphonic acid molecule to the corresponding amine: in each compound the aggregation of the resulting phenylphosphonate anions retains just one of the motifs observed in phenylphosphonic acid itself (Weakley, 1976).

3.1.1. *Compound (1).* The asymmetric unit of (1), $C_{10}H_9N_2.[C_6H_5PO_2(OH)]$, contains one phenylphosphonate anion and one singly protonated 4,4′-bipyridyl unit, which are linked by N—H···O and C—H···O hydrogen bonds in a motif with unitary and binary graph-set descriptors $N_1 = DD$, $N_2 = R_2^2(7)$ (Fig. 1); a rather similar $R_2^2(7)$ synthon (Desiraju, 1995), although without proton transfer from acid to amine, has been observed in an adduct of 4,4′-bipyridyl with 1,3,5-benzenetricarboxylic acid (Sharma & Zaworotko,

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0379). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

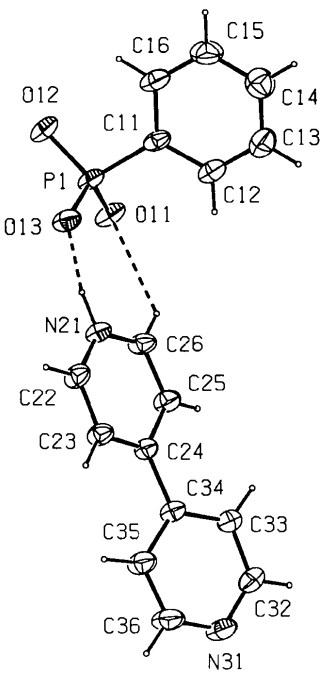


Fig. 1. The asymmetric unit of (1), showing the atom-numbering scheme and the $R_2^2(7)$ synthon connecting the two components. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{16}H_{15}N_2O_3P$	$C_{16}H_{24}N_2O_6P_2$	$C_{18}H_{26}N_2O_6P_2$
Chemical formula weight	314.27	402.31	428.35
Cell setting	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	6.9026 (8)	6.0042 (9)	6.3607 (3)
b (Å)	9.7086 (9)	19.746 (3)	21.8300 (11)
c (Å)	12.201 (2)	8.651 (2)	14.5965 (9)
α (°)		77.138 (9)	
β (°)	74.345 (10)	105.63 (2)	92.558 (6)
γ (°)		75.477 (8)	
V (Å^3)	751.6 (2)	987.7 (3)	2024.8 (2)
Z	2	2	4
D_x (Mg m^{-3})	1.389	1.353	1.405
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25
θ range (°)	9.30–18.97	7.90–17.15	10.02–20.58
μ (mm^{-1})	0.197	0.254	0.252
Temperature (K)	294 (1)	294 (1)	294 (1)
Crystal form	Block	Block	Plate
Crystal size (mm)	0.42 × 0.29 × 0.19	0.42 × 0.19 × 0.05	0.42 × 0.31 × 0.02
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	Empirical, φ scans at 4° steps (North *et al.*, 1968)	Gaussian (North *et al.*, 1968)	Gaussian (North *et al.*, 1968)
T_{min}	0.9102	0.9551	0.9285
T_{max}	0.9994	0.9860	0.9610
No. of measured reflections	3420	2538	3629
No. of independent reflections	3418	1747	3198
No. of observed reflections	2474	1063	2438
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.050	0.020	0.008
θ_{max} (°)	27.37	25.00	25.00
Range of h, k, l	$-8 \rightarrow h \rightarrow 8$ $0 \rightarrow k \rightarrow 12$ $-15 \rightarrow l \rightarrow 15$	$-7 \rightarrow h \rightarrow 7$ $0 \rightarrow k \rightarrow 25$ $0 \rightarrow l \rightarrow 11$	$-6 \rightarrow h \rightarrow 6$ $0 \rightarrow k \rightarrow 25$ $0 \rightarrow l \rightarrow 17$
No. of standard reflections	3	3	3
Frequency of standard reflections (min)	120	120	120
Intensity decay (%)	No decay, variation 2.5	No decay, variation 3.0	No decay, variation 0.4
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0465	0.0565	0.0377
$wR(F^2)$	0.1250	0.1339	0.0939
S	1.192	1.121	1.122
No. of reflections used in refinement	3418	1747	3198
No. of parameters used	202	120	258
H-atom treatment	H parameters constrained	H parameters constrained	H parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.1437P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.9750P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	−0.002	0.002	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.267	0.307	0.346
$\Delta\rho_{min}$ (e Å^{-3})	−0.265	−0.472	−0.223
Extinction method	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient	0.0169 (42)	0.0167 (42)	0.0025 (8)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)

Table 1 (*cont.*)

	(1)	(2)	(3)
Computer programs			
Data collection	*CAD*-4 (Enraf–Nonius, 1992)	*CAD*-4 (Enraf–Nonius, 1992)	*CAD*-4 (Enraf–Nonius, 1992)
Cell refinement	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* (Enraf–Nonius, 1992)
Data reduction	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)
Structure solution	*SOLVER* in *NRCVAX*96	*SOLVER* in *NRCVAX*96	*SOLVER* in *NRCVAX*96
Structure refinement	*NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993)	*NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993)	*NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997)	*NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997)	*NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997)

1996). Pairs of the asymmetric units in (1) related by centres of inversion form dimers based upon the $R_2^2(8)$ $[P(O)OH]_2$ ring (Fig. 2). There are no hydrogen bonds of any kind involving the remote N31 atom. These dimeric units are linked by multiple C—H···O hydrogen bonds into chains running parallel to the [010] direction. C22 of the bipyridyl at (x, y, z) acts as a donor, in a three-centre hydrogen bond, to both O12 and O13 in the phosphonate anion at ($-x$, 1 − y, $-z$; Fig. 2 and Table 3); propagation of this interaction by the centres of inversion generates the [010] chain and two new ring motifs of types $R_4^2(10)$ and $R_1^2(4)$. Each supramolecular aggregate thus consists of a linear stem built from O—H···O, N—H···O and C—H···O hydrogen bonds, with pendent phenyl and bipyridyl units arranged in an alternate fashion, like leaves attached to the stem (Fig. 2).

3.1.2. *Compound (2).* This salt has the constitution $C_4H_{12}N_2.[C_6H_5PO_2OH]_2$, resulting from the complete transfer of one proton from each molecule of the acid onto the amine, which is thus doubly protonated. The asymmetric unit contains one anion and half a cation (Fig. 3), and the structure consists of anion dimers and piperazinium dications, each lying across centres of inversion (Fig. 4). The phenylphosphonate anions are linked by O—H···O hydrogen bonds into centrosymmetric $R_2^2(8)$ dimers and each cation forms N—H···O hydrogen bonds to four different anion dimers. Thus, the cation centred at the origin acts as a donor to the anion dimers at ($\pm\frac{1}{2}$, 0, $\pm\frac{1}{2}$), while the anion dimer at ($\frac{1}{2}$,

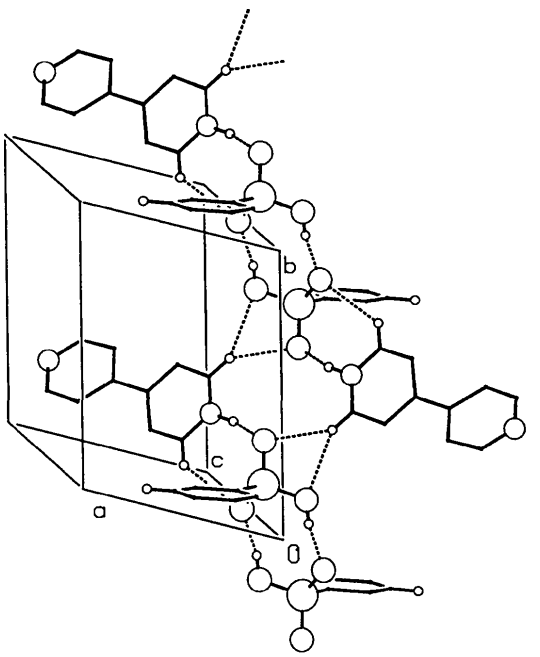


Fig. 2. View of part of the crystal structure of (1), showing the chain running parallel to [010].

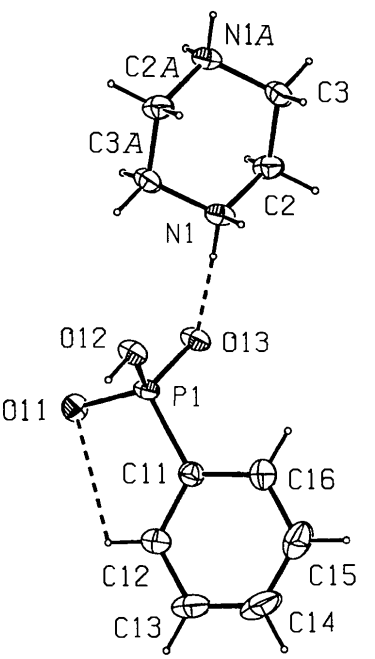


Fig. 3. The molecular aggregate of (2), showing the atom-numbering scheme. Atoms are depicted as in Fig. 1.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
(1)				
P1	0.12201 (8)	0.18433 (5)	−0.07315 (5)	0.0454 (2)
O11	0.1962 (2)	0.0648 (2)	0.01939 (14)	0.0555 (4)
O12	−0.0855 (2)	0.1716 (2)	−0.09156 (14)	0.0547 (4)
O13	0.1065 (2)	0.33274 (15)	−0.04913 (14)	0.0548 (4)
C11	0.3055 (3)	0.1634 (2)	−0.2079 (2)	0.0446 (5)
C12	0.5146 (3)	0.1384 (2)	−0.2122 (2)	0.0534 (5)
C13	0.6575 (4)	0.1253 (3)	−0.3144 (3)	0.0672 (7)
C14	0.5955 (5)	0.1362 (3)	−0.4147 (3)	0.0746 (7)
C15	0.3905 (5)	0.1612 (3)	−0.4124 (2)	0.0758 (8)
C16	0.2455 (4)	0.1755 (3)	−0.3104 (2)	0.0603 (6)
N21	0.3223 (3)	0.3586 (2)	0.0836 (2)	0.0467 (4)
C22	0.3139 (3)	0.4783 (2)	0.1227 (2)	0.0511 (5)
C23	0.4477 (3)	0.4808 (2)	0.1875 (2)	0.0494 (5)
C24	0.5918 (3)	0.3575 (2)	0.2147 (2)	0.0410 (4)
C25	0.5933 (3)	0.2346 (2)	0.1730 (2)	0.0509 (5)
C26	0.4581 (4)	0.2389 (2)	0.1076 (2)	0.0521 (5)
N31	1.0111 (3)	0.3449 (2)	0.4223 (2)	0.0663 (6)
C32	1.0468 (4)	0.2504 (3)	0.3516 (2)	0.0630 (6)
C33	0.9175 (3)	0.2507 (3)	0.2826 (2)	0.0541 (5)
C34	0.7383 (3)	0.3546 (2)	0.2849 (2)	0.0438 (5)
C35	0.7013 (4)	0.4543 (2)	0.3577 (2)	0.0600 (6)
C36	0.8411 (4)	0.4445 (3)	0.4229 (2)	0.0703 (7)
(2)				
P1	−0.4521 (2)	−0.07758 (5)	0.35202 (11)	0.0321 (3)
O11	−0.6805 (4)	−0.04390 (13)	0.3433 (3)	0.0398 (7)
O12	−0.2484 (5)	−0.02690 (14)	0.4189 (3)	0.0411 (7)
O13	−0.4211 (5)	−0.10362 (13)	0.1974 (3)	0.0424 (8)
C11	−0.4140 (7)	−0.1441 (2)	0.4984 (4)	0.0365 (9)
C12	−0.5601 (8)	−0.1510 (2)	0.5970 (5)	0.0591 (13)
C13	−0.5267 (12)	−0.2016 (3)	0.7099 (7)	0.089 (2)
C14	−0.3517 (13)	−0.2464 (3)	0.7243 (8)	0.096 (2)
C15	−0.2020 (11)	−0.2414 (3)	0.6306 (7)	0.081 (2)
C16	−0.2340 (9)	−0.1903 (2)	0.5173 (6)	0.0607 (13)
N1	−0.0783 (5)	−0.0420 (2)	0.1089 (3)	0.0387 (8)
C2	−0.0553 (8)	−0.0694 (2)	−0.0450 (5)	0.0460 (11)
C3	0.1321 (8)	−0.0315 (2)	−0.0969 (5)	0.0450 (11)
(3)				
P1	0.81425 (11)	0.27359 (3)	0.27773 (4)	0.0323 (2)
O11	0.6137 (3)	0.24057 (9)	0.29613 (15)	0.0544 (6)
O12	0.9844 (3)	0.23251 (9)	0.23688 (12)	0.0473 (5)
O13	0.7797 (3)	0.32715 (8)	0.21324 (12)	0.0456 (5)
C11	0.9219 (4)	0.30318 (10)	0.3853 (2)	0.0322 (6)
C12	0.7892 (5)	0.33607 (13)	0.4407 (2)	0.0473 (7)
C13	0.8595 (6)	0.35916 (15)	0.5243 (2)	0.0590 (9)
C14	1.0644 (6)	0.34954 (13)	0.5548 (2)	0.0555 (9)
C15	1.1983 (5)	0.31750 (13)	0.5014 (2)	0.0499 (8)
C16	1.1292 (4)	0.29454 (11)	0.4166 (2)	0.0379 (6)
P2	−0.18958 (10)	0.39647 (3)	−0.17262 (4)	0.0294 (2)
O21	−0.3595 (3)	0.35015 (8)	−0.16294 (12)	0.0427 (5)
O22	0.0223 (3)	0.36971 (9)	−0.20195 (15)	0.0505 (5)
O23	−0.1490 (3)	0.43407 (7)	−0.08613 (11)	0.0360 (4)
C21	−0.2651 (4)	0.44961 (10)	−0.26298 (15)	0.0285 (6)
C22	−0.4735 (4)	0.45525 (13)	−0.2939 (2)	0.0414 (7)
C23	−0.5273 (5)	0.49692 (15)	−0.3632 (2)	0.0524 (8)
C24	−0.3770 (5)	0.53266 (13)	−0.4005 (2)	0.0493 (8)
C25	−0.1707 (5)	0.52739 (13)	−0.3709 (2)	0.0463 (7)
C26	−0.1146 (4)	0.48594 (11)	−0.3022 (2)	0.0374 (6)
N1	0.4392 (3)	0.35297 (10)	0.12537 (13)	0.0358 (5)
N2	0.1390 (3)	0.39063 (9)	0.02566 (13)	0.0326 (5)
C1	0.3209 (5)	0.29945 (13)	0.0870 (2)	0.0558 (8)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C2	0.1317 (5)	0.32246 (12)	0.0291 (2)	0.0498 (8)
C3	0.5194 (5)	0.3905 (2)	0.0513 (2)	0.0736 (12)
C4	0.3358 (4)	0.4124 (2)	−0.0110 (2)	0.0593 (9)
C5	0.2979 (5)	0.38832 (14)	0.1815 (2)	0.0469 (7)
C6	0.1187 (4)	0.41461 (12)	0.1202 (2)	0.0376 (6)

0, $\frac{1}{2}$) is an acceptor of N—H···O hydrogen bonds from cations centred at the origin and at (1, 0, 0), (0, 0, 1) and (1, 0, 1). Each phenylphosphonate anion acts as a donor in one O—H···O hydrogen bond, as an acceptor in another and as an acceptor in two N—H···O hydrogen bonds. The structure thus forms hydrogen-bonded sheets in which both the components, cations and anion dimers, are cyclic. The sheets contain two further types of ring formed by the N—H···O hydrogen bonds: the ring centred at (0, 0, $\frac{1}{2}$) has unitary and binary level graph sets $N_1 = DDD$, $N_2 = R_6^4(16)$, while that centred at ($\frac{1}{2}$, 0, 0) has $N_1 = DD$, $N_2 = R_4^4(18)$. Compound (2) also contains C—H···O hydrogen bonds (Table 3). In addition to an intramolecular hydrogen bond, graph set $S(5)$, within the phenylphosphonate anion (Fig. 3) there is an intermolecular bond with C3 in the cation at (x, y, z) acting as a donor towards O13 in the phosphonate anion at (1 + x, y, z): this and the inversion-generated C—H···O hydrogen bond have the effect of reinforcing the N—H···O hydrogen bonds and of sub-dividing the $R_4^4(18)$ rings into one $R_4^2(10)$ and two $R_2^2(8)$ rings. Between neighbouring sheets there are no contact distances less than the sum of the van der Waals' radii.

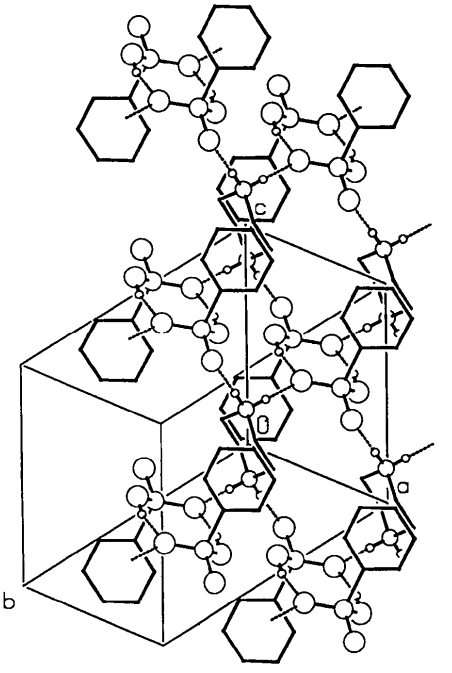


Fig. 4. View of part of the crystal structure of (2), showing the formation of sheets parallel to (010).

Table 3. *Selected molecular dimensions (Å, °)*

(*a*) Phosphonate anions

	(1)	(2)	(3)	
	n = 1	*n* = 1	*n* = 1	*n* = 2
P*n*—O*n*1	1.5213 (15)	1.508 (3)	1.500 (2)	1.491 (2)
P*n*—O*n*2	1.5467 (14)	1.565 (3)	1.546 (2)	1.547 (2)
P*n*—O*n*3	1.5058 (14)	1.491 (3)	1.511 (2)	1.518 (2)
P*n*—C*n*1	1.801 (2)	1.796 (4)	1.804 (2)	1.805 (2)
O*n*1—P*n*—O*n*2	112.02 (9)	110.3 (2)	113.96 (12)	114.48 (11)
O*n*2—P*n*—O*n*3	109.89 (8)	106.1 (2)	107.07 (11)	108.45 (11)
O*n*3—P*n*—O*n*1	112.74 (9)	116.0 (2)	112.46 (11)	112.63 (10)
O*n*1—P*n*—C*n*1	107.73 (9)	107.4 (2)	108.01 (12)	109.54 (11)
O*n*2—P*n*—C*n*1	106.09 (9)	105.6 (2)	107.35 (11)	104.31 (11)
O*n*3—P*n*—C*n*1	108.04 (9)	111.0 (2)	107.70 (11)	106.86 (10)
C*n*2—C*n*1—P*n*—O*n*1	−46.0 (2)	−9.4 (4)	−49.5 (2)	18.3 (2)
C*n*2—C*n*1—P*n*—O*n*2	−166.1 (2)	108.2 (4)	−172.8 (2)	141.3 (2)
C*n*2—C*n*1—P*n*—O*n*3	76.1 (2)	−137.2 (4)	72.2 (2)	−104.0 (2)

(*b*) Amine cations

(1)			
N21—C22	1.334 (3)	N31—C32	1.330 (3)
N21—C26	1.328 (3)	N31—C36	1.320 (3)
Inter-ring dihedral angle	20.5 (1)		
(2)			
N1—C2	1.477 (5)	N1—C3^{i}	1.485 (5)
C2—C3	1.516 (5)		
(3)			
N1—C1	1.486 (3)	N2—C2	1.490 (3)
N1—C3	1.466 (3)	N2—C4	1.463 (3)
N1—C5	1.463 (3)	N2—C6	1.487 (3)
C1—C2	1.524 (4)	N1—C1—C2—N2	3.9 (3)
C3—C4	1.524 (4)	N1—C3—C4—N2	2.0 (4)
C5—C6	1.529 (4)	N1—C5—C6—N2	5.0 (3)

(*c*) Hydrogen bonds

(1)			
O12···O11^{i}	2.497 (3)	O12—H12···O11^{i}	167
N21···O13	2.565 (3)	N21—H21···O13	169
C22···O12^{ii}	3.350 (3)	C22—H22···O12^{ii}	151
C22···O13^{ii}	3.258 (3)	C22—H22···O13^{ii}	148
C26···O11	3.268 (3)	C26—H26···O11	134
(2)			
N1···O11^{iii}	2.685 (4)	N1—H1*A*···O11^{iii}	168
N1···O13	2.673 (4)	N1—H1*B*···O13	177
O12···O11^{iv}	2.616 (4)	O12—H12···O11^{iv}	159
C3···O13^{iii}	3.469 (5)	C3—H3*A*···O13^{iii}	156
C12···O11	2.993 (5)	C12—H12*A*···O11	106
(3)			
N1···O13	2.531 (3)	N1—H1···O13	166
N2···O23	2.579 (3)	N2—H2···O23	172
O12···O21^{v}	2.500 (3)	O12—H12···O21^{v}	165
O22···O11^{vi}	2.477 (3)	O22—H22···O11^{vi}	156
C1···O12^{vii}	3.453 (4)	C1—H1*A*···O12^{vii}	152
C4···O21^{iii}	3.302 (4)	C4—H4*B*···O21^{iii}	137
C6···O13^{vii}	3.225 (3)	C6—H6*A*···O13^{vii}	148
C6···O23^{ii}	3.347 (3)	C6—H6*B*···O23^{ii}	168

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, -z$; (iii) $1+x, y, z$; (iv) $-1-x, -y, 1-z$; (v) $\frac{3}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vii) $-1+x, y, z$

3.1.3. *Compound (3).* In the adduct (3), formed between phenylphosphonic acid and DABCO, the asymmetric unit contains two independent phenylphosphonate units and one DABCO (Fig. 5). There is complete transfer of a proton from O13 in one molecule of the acid to N1 of the DABCO, but the proton transfer to N2 from O23 in the second acid molecule is incomplete: the site occupation factors for the H atoms bonded to N2 and O23 refined to 0.68 (4) and 0.32 (4), respectively. The structure of (3) will be described in terms of the major tautomer containing doubly protonated DABCO, $C_6H_{14}N_2.[C_6H_5PO_2OH]_2$. The phenylphosphonate anions are linked into continuous chains parallel to the [100] direction by short O—H···O hydrogen bonds (Fig. 6): O12 in the unit at (x, y, z) acts as a hydrogen-bond donor to O21 in the unit at $(\frac{3}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, while O22 in this latter unit acts as a hydrogen-bond donor to O11 in the unit at $(1 + x, y, z)$. The chains parallel to the [100] direction thus contain both the independent phosphonate anions, which occur alternately, and the hydrogen bonds in this chain are all of O—H···O^- type between one neutral and one charged oxygen. Pairs of such [100] chains related by the *n* glide planes are cross-linked by the DABCO dications to generate a second set of chains running parallel to the [201] direction (Fig. 7). Each anion in the major tautomer therefore acts as a donor in one O—H···O hydrogen bond, as an acceptor in another and as an acceptor of an N—H···O hydrogen bond: in the minor tautomer, the latter is replaced by an O—H···N hydrogen bond in which the phenylphosphonate anion acts as the donor rather than as the acceptor. The pattern of the cross-linking is such that successive DABCO units attached to any given chain lie on alternate sides of that chain, so that all the chains generated by the successive actions of *n* glide planes are connected into a continuous sheet lying parallel to the (010) plane. Further parallel sheets are generated by the action of the inversion centres. The hydrogen-bond

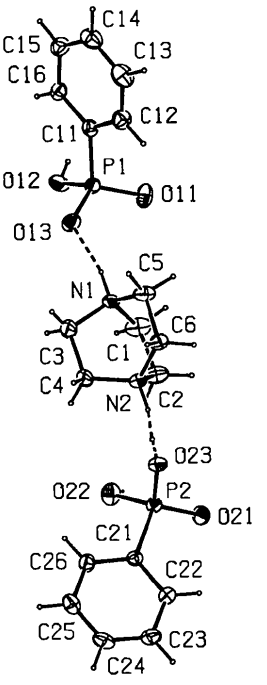


Fig. 5. The asymmetric unit of (3), showing the disorder of one of the H atoms. Atoms are depicted as in Fig. 1.

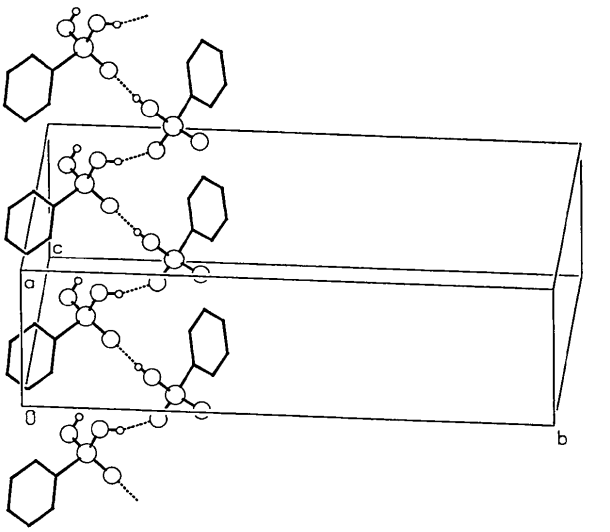


Fig. 6. View of part of the crystal structure of (3), showing the formation of chains parallel to [100]: H atoms bonded to carbon are omitted for the sake of clarity.

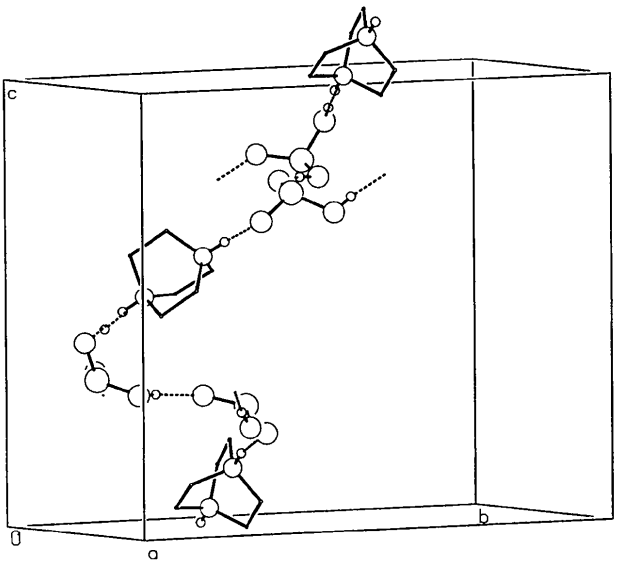


Fig. 7. View of part of the crystal structure of (3), showing the formation of chains parallel to [201]: phenyl rings and H atoms bonded to carbon are omitted for the sake of clarity.

motifs in the [100] chains have graph sets $N_1 = DD$, $N_2 = C_2^2(8)$, while for the [201] chains, where there are actually only three independent types of hydrogen bond, $N_1 = DDD$, $N_2 = C_5^5(22)$; the intersection of the [100] and [201] chains gives rise to sheets built from $R_8^8(34)$ rings (Fig. 8). This topology of chains built from O—H···O hydrogen bonds and cross-linked into sheets by an amine spacer is precisely that found in the 1:2 adduct of DABCO with 4,4′-thiodiphenol, where the intersection of $C(12)$ and $C_3^3(9)$ chains gives sheets built from $R_8^8(62)$ rings (Ferguson *et al.*, 1997).

The $R_8^8(34)$ rings in (3) are sub-divided by C—H···O hydrogen bonds (Fig. 8, Table 3) into $R_2^2(9)$, $R_4^3(13)$, $R_4^4(13)$ and $R_4^4(16)$ sectors. C1 and C6 in the DABCO cation at (x, y, z) act as donors to O12 and O13 in the phosphonate anion at $(-1 + x, y, z)$, while C4 in the DABCO at (x, y, z) acts as a donor to O21 in the phosphonate anion at $(1 + x, y, z)$. In addition, there is a C—H···O hydrogen bond between C6 in the DABCO cation at (x, y, z) and O23 of the phosphonate anion at $(-x, 1 - y, -z)$, whose repetition throughout the structure has the effect of linking all the sheets together into a continuous three-dimensional framework.

Compounds (1) and (2) thus both retain the $R_2^2(8)$ dimer motif observed in phenylphosphonic acid, while (3) retains the $C(4)$ chain motif. The overall supramolecular architectures in (1), (2) and (3) are thus based upon a one-dimensional string, a two-dimensional sheet and a three-dimensional framework, respectively.

3.2. *Molecular dimensions and conformations*

3.2.1. *Phenylphosphonate anions.* In each of the independent phenylphosphonate anions (Table 3), the P—C distance is significantly greater than the 1.773 (5) Å observed in phenylphosphonic acid (Weakley, 1976), presumably as a direct consequence of the overall negative charge. The P—O distances in each of (1)–(3) show a clear distinction between those involving P—O(H), P*n*—O*n*2 (*n* = 1 or 2) and those in the formally charged $[PO_2]^-$ fragment, P*n*—O*n*1 and P*n*—O*n*3, comparable with the difference between P=O and P—O(H) in the free acid. Both the neutral phenylphosphonic acid and its mono-anion are present in the structure of $[(PPh_2Me)_2Pt(\mu\text{-}PPhH)\text{-}Pt(PPh_2Me)_2].(Cl)_2.[PhPO_2(OH)]_2.[PhPO(OH)_2]_2$, but the metrical precision of the structure determination was compromised by the severe crystal decay resulting in a reduction in diffraction intensity of around 50% (Parkin *et al.*, 1990).

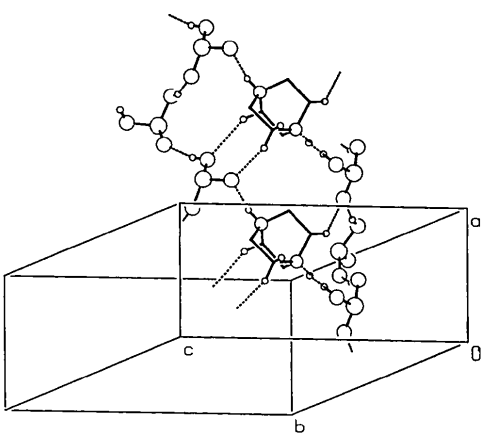


Fig. 8. View of part of the crystal structure of (3), showing the formation of $R_8^8(34)$ rings, sub-divided into $R_2^2(9)$, $R_4^3(13)$, $R_4^4(13)$ and $R_4^4(16)$ sectors: phenyl rings and H atoms bonded to carbon are omitted for the sake of clarity.

As in the free acid, the C—P—O(H) angle is systematically smaller than the tetrahedral value. The conformations of the phenylphosphonate anions, as judged from the C—C—P—O torsional angles (Table 3), vary widely between the different salts: one of the two independent anions in (3) has a conformation very similar to that in (1), but otherwise there are no similarities.

3.2.2. *Amine cations.* The C—N distances in the piperazine cation in (2) are closer to those observed in the salt-forming 1:2 adduct of piperazine with 4,4′-sulfonyldiphenol, 1.477 (3) Å (Coupar *et al.*, 1996*a*), than to those in the neutral 1:1 adduct of piperazine with 4,4′-thiodiphenol, 1.460 (3) and 1.462 (3) Å (Coupar *et al.*, 1996*b*); as usual, protonation at nitrogen leads to an increase in the C—N bond lengths.

Although in (3) there is partial disorder of one of the protons transferred to the DABCO, such that protonation of N2 is incomplete (as judged from difference maps and subsequent refinement of the site occupation factors), there is no orientational disorder of the DABCO skeleton, such as is found in the DABCO adducts with 4,4′-oxodiphenol and 4,4′-thiodiphenol (Ferguson *et al.*, 1997). The C—N distances in the protonated DABCO component in (3) range from 1.463 (3) to 1.490 (3) Å with mean 1.476 (11) Å; by comparison, in the 1:1 adduct of DABCO with 4,4′-isopropylidenediphenol, where there is neither proton transfer from the bis-phenol to DABCO nor orientational disorder of the DABCO skeleton, the C—N distances range from 1.452 (4) to 1.461 (4) Å, with mean 1.458 (4) Å (Ferguson *et al.*, 1997). Again, protonation at nitrogen leads to a small, but significant, increase in the adjacent C—N bond lengths.

The conformational properties of the DABCO molecule have been extensively investigated, both in the solid state (Weiss *et al.*, 1964; Nimmo & Lucas, 1976; Mak *et al.*, 1984) and in the gas phase (Yokozeki & Kuchitsu, 1971). The principal point of interest is the extent of any twist of the molecule from ideal D_{3h} symmetry by internal rotation about the N···N vector: in the D_{3h} conformation, the neighbouring CH_2 groups are all eclipsed. For isolated molecules in the gas phase (Yokozeki & Kuchitsu, 1971), the internal dynamics

indicated a very broad potential well for the twist motion, best fitted by an harmonic-quartic potential function having an energy minimum corresponding to a twist of *ca.* 10° from the D_{3h} geometry. In (3) the N—C—C—N torsion angles range from 2.0 (4) to 5.0 (3)°, indicative of a small but real distortion of the DABCO skeleton from the fully eclipsed conformation. Distortions of a similar magnitude have been observed in the 2:1 adduct of phenol with DABCO and in the 1:1 adduct of hydroquinone with DABCO (Mak *et al.*, 1984).

3.2.3. *Hydrogen bonds.* In (1)–(3) all the O—H···O and N—H···O hydrogen bonds are short (Table 3), reflecting the fact that all, except for the minor tautomer of the O23···N2 bond in (3), involve charged components (Gilli *et al.*, 1994). Although some of the O···O distances fall in the range where centred hydrogen bonds are commonly found, examination of difference maps showed clearly that all the hydrogen bonds in (1)–(3) are unsymmetrical: this conclusion is confirmed by the clear difference between the P—O^- and P—O(H) bond lengths §3.2.1 (Table 3); the two independent P—O distances would be expected to be essentially identical in a centred hydrogen bond of the type P—O···H···O—P.

4. General comments

The failure of N31 in (1) to participate in any hydrogen bonds, although at first sight surprising, is not without precedent. In the 1:1 adduct formed between 4,4′-bipyridyl and ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe(C_5H_4CPh_2OH)_2]$, half of the bipyridyl molecules are connected to the ferrocenediol units by means of O—H···N hydrogen bonds, while the other half reside in cavities in the structure and are unconnected to any of the other molecular components (Glidewell *et al.*, 1994). The inactivity of the bipyridyl N atoms in hydrogen-bond formation arises from a mismatch between the numbers of hydrogen-bond donors and acceptors capable of forming hard hydrogen bonds (Braga *et al.*, 1995) in these systems.

In (1) there is an excess of such acceptors, assuming the total number of donors to equal the number of O—H and N—H bonds: in a 1:1 adduct there are two donors per asymmetric unit of (1), against a total of three acceptors, even if each unprotonated O atom acts as only a single acceptor. Similarly, in the 1:1 adduct of 4,4′-bipyridyl with ferrocene-1,1′-diylbis(diphenylmethanol) the asymmetric unit contains twice as many acceptors as donors. In (2) the numbers of donors and acceptors can be matched precisely for a 2:1 stoichiometry, provided that one unprotonated oxygen in each acid unit acts as a double acceptor, as observed for O11, while in (3) the numbers of hydrogen-bond donors and acceptors match precisely when each unprotonated oxygen acts as a single acceptor.

An excess of hydrogen-bond acceptors *X* is often associated with the formation of soft (Braga *et al.*, 1995) hydrogen bonds of the type C—H···*X* (Hunter, 1991; Hanton *et al.*, 1992). Excellent examples of this precept are found in the structures of cyanoferrocene (Bell *et al.*, 1996) and ferrocene-1,1′-diylbis(2-phenylethanedione) (Ferguson *et al.*, 1996); in neither of these systems are there any conventional hydrogen-bond donors at all, but their molecules are nonetheless linked, by C—H···N hydrogen bonds in the one case and C—H···O hydrogen bonds in the other, into continuous two- and three-dimensional networks, respectively. Compound (1) shows no evidence for C—H···N hydrogen-bond formation, although C—H···O interactions are present in profusion.

GF thanks NSERC (Canada) for research grants; RMG thanks EPSRC (UK) for financial support.

References

Bell, W., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 1928–1930.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Braga, D., Grepioni, F., Biradha, K., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.

Bruno, G. & Randaccio, L. (1980). *Acta Cryst.* B**36**, 1711–1712.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996*a*). *Acta Cryst.* C**52**, 3052–3055.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996*b*). *Acta Cryst.* C**52**, 3055–3057.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Enraf–Nonius (1992). *CAD-4-PC Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Ferguson, G. (1997). *PRPCIF97. A WordPerfect5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs.* University of Guelph, Canada.

Ferguson, G., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 513–520.

Ferguson, G., Glidewell, C., Royles, B. J. L. & Smith, D. M. (1996). *Acta Cryst.* C**52**, 2465–2468.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (1994). *J. Am. Chem. Soc.* **116**, 909–915.

Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1971–1982.

Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.

Hunter, C. A. (1991). *J. Chem. Soc. Chem. Commun.* pp. 749–751.

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

Jones, R. E. & Templeton, D. H. (1958). *Acta Cryst.* **11**, 484–487.

Jönsson, P.-G. (1971). *Acta Cryst.* B**27**, 893–898.

Mak, T. C. W., Yip, W.-H. & Book, L. (1984). *J. Cryst. Spectrosc. Res.* **14**, 457–465.
Nahringbauer, I. (1970). *Acta Chem. Scand.* **24**, 453–462.
Nimmo, J. K. & Lucas, B. W. (1976). *Acta Cryst.* B**32**, 348–353.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Parkin, I. V., Slawin, A. M. Z., Williams, D. J. & Woollins, J. D. (1990). *Inorg. Chim. Acta*, **172**, 159–163.
Sharma, C. V. K. & Zaworotko, M. J. (1996). *Chem. Commun.* pp. 2655–2656.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sim, G. A., Robertson, J. M. & Goodwin, T. H. (1955). *Acta Cryst.* **8**, 157–164.
Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program*. July 1995 Version. University of Utrecht, The Netherlands.
Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program*. July 1995 Version. University of Utrecht, The Netherlands.
Weakley, T. J. R. (1976). *Acta Cryst.* B**32**, 2889–2890.
Weiss, G. S., Parkes, A. S., Nixon, E. R. & Hughes, R. E. (1964). *J. Chem. Phys.* **41**, 3759–3767.
Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.
Yokozeki, A. & Kuchitsu, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 72–77.