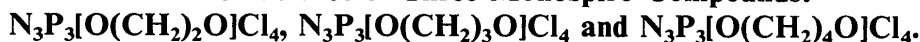EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1982). *Acta Cryst.* B38, 140–149.

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Structural Investigations of Phosphorus–Nitrogen Compounds.
1. The Structures of Three Monospiro Compounds: $N_3P_3[O(CH_2)_2O]Cl_4$, $N_3P_3[O(CH_2)_3O]Cl_4$ and $N_3P_3[O(CH_2)_4O]Cl_4$.
The Relationship of OPO Bond Angles in PO_2N_2 Tetrahedra with ^{31}P Chemical Shifts*

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Abstract

The crystal structures of three dioxyalkane mono-spiro compounds {2,2-ethylenedioxy-4,4,6,6-tetra-chlorocyclotriphosphazatriene, $N_3P_3[O(CH_2)_2O]Cl_4$ (1), 2,2-trimethylenedioxy-4,4,6,6-tetrachlorocyclo-triphosphazatriene, $N_3P_3[O(CH_2)_3O]Cl_4$ (2), and 2,2-tetramethylenedioxy-4,4,6,6-tetrachlorocyclotri-phosphazatriene, $N_3P_3[O(CH_2)_4O]Cl_4$ (3)} have been determined by X-ray analysis. [Crystal data: (1): triclinic, $P\bar{1}$, $a = 7.763$ (2), $b = 8.008$ (2), $c = 10.352$ (3) Å, $\alpha = 99.38$ (2), $\beta = 93.95$ (2), $\gamma = 110.83$ (2)°, $Z = 2$; (2): orthorhombic, $Cmc2_1$, $a = 10.650$ (2), $b = 13.457$ (2), $c = 8.833$ (2) Å, $Z = 4$; (3): monoclinic, $C2/c$, $a = 10.733$ (3), $b = 13.646$ (3), $c = 9.099$ (1) Å, $\beta = 93.39$ (2)°, $Z = 4$.] For structure solutions direct methods [*SHELX* 76 (1), *SHELX* 84 (2)] and Patterson methods (3) were used. Full-matrix least-squares refinements led to R values of 5.6% for (1), 3.3% for (2) and 4.1% for (3) using 2052, 588, and 1324 unique reflections respectively [$F_o > 3\sigma(F_o)$]. The cyclotriphosphazatriene moiety is essentially planar in all three compounds. The bond lengths and angles of this ring show the expected effects of replacing two Cl atoms by the more electron-releasing alkoxy groups. However, the data show no

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*Presented in part at the International Conference on Phosphorus Chemistry, Nice, France, September 1983. [The chemical nomenclature used throughout this paper conforms to that established by Shaw, Fitzsimmons & Smith (1962) and differs from current IUPAC recommendations.]

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Table 1. *Selected* ^{31}P *and* ^{1}H *NMR spectroscopic data of compounds* (1)–(3)

Compound	δP(spiro)	δPCl_2	^2J(PP) (Hz)	^3J(PH) (Hz)
(1)	23·8	25·5	67·0	11·2
(2)	2·4	23·3	69·2	12·8
(3)	9·2	22·8	71·0	18·2

significant differences in the phosphazene rings of these three compounds. All the structural differences are confined to the phosphate rings which, not unexpectedly, show major differences in OPO and POC angles and minor ones in P–O bond lengths. The phosphate rings have a twist boat (1), a chair (2) and an unusual chair conformation (3); in the latter five atoms are coplanar. A relationship between OPO bond angles in PO_2N_2 tetrahedra and ^{31}P chemical shifts has been deduced.

Introduction

The present paper is the first of a series devoted to structural studies on related phosphorus–nitrogen compounds. It is hoped to discover how structural parameters relate to changes observed by other physicochemical techniques, such as NMR and NQR spectroscopy, basicity measurements, *etc.*, as well as to the chemical behaviour of these compounds.

We report here the structures of three dioxyalkane monospiro compounds.

A preliminary report has been made at the International Conference on Phosphorus Compounds (Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1983).

The preparation and NMR spectroscopic properties of these compounds have been reported elsewhere (Contractor, Parkes, Shaw & Yılmaz, 1984). We note the drastic changes in the ^{31}P chemical shifts of the spiro P nuclei, as well as the relatively high values for the PCl_2 groups which usually fall in the region of δ 18–22 (Keat, Shaw & Woods, 1976). We further note the distinct changes in ^3J(PH) coupling constants when the OCH_2 groups are part of 5-, 6-, and 7-membered phosphate rings (see data summarized in Table 1).

Experimental

Crystals were grown as follows: (1) from methylene chloride, m.p. 439–440 K; (2) from diethyl ether, m.p. 429–430 K; (3) from methylene chloride, m.p. 429–430 K. A mixed m.p. of compounds (2) and (3) showed a strong depression. The similarities in melting points and in unit-cell dimensions of compounds (2) and (3) are noteworthy. All the crystals were colourless and block-shaped. Densities were measured by the flotation method. Unit-cell parameters were determined by least-squares refinement

Table 2. *Additional crystal data and experimental information*

	(1)	(2)	(3)
M_r	336·81	350·83	364·86
$V(\text{Å}^3)$	587·78	1264·30	1330·28
$D_m(\text{g cm}^{-3})$	1·891	1·820	1·807
$D_x(\text{g cm}^{-3})$	1·902	1·843	1·821
$\mu(\text{Mo } K\alpha)(\text{cm}^{-1})$	12·83	11·95	11·38
Crystal size (mm)	0·30 ×0·20 × 0·25	0·50 ×0·25 × 0·25	0·40 ×0·20× 0·25
Total unique data	2555	655	1450
Max. Δ/σ in final least-squares cycle	0·1	0·005	0·05
Least-squares parameters	143	92	90
$(\Delta\rho)_{max}(\text{e Å}^{-3})$	≤0·7	≤0·3	≤0·5
Weights	$[\sigma^2(F_o)+ 0.0006F_o^2]^{-1}$	$[\sigma^2(F_o)+ 0.0005F_o^2]^{-1}$	$[\sigma^2(F_o)+ 0.0001F_o^2]^{-1}$

of the setting angles for 25 reflections [$16 < \theta(\text{Mo } K\alpha) < 17°$] automatically centred on an Enraf–Nonius CAD-4 diffractometer. Intensity data were recorded on the same instrument at 295(2) K, using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å; graphite-monochromatized), in the $\omega/2\theta$ scan mode, in a manner previously described in detail (Hursthouse, Jones, Malik & Wilkinson, 1979), with a θ range of 1·5 to 25°. Data for all the compounds were corrected for Lorentz and polarization effects. Additional crystal data and experimental information are given in Table 2.

(1)   (2)   (3)
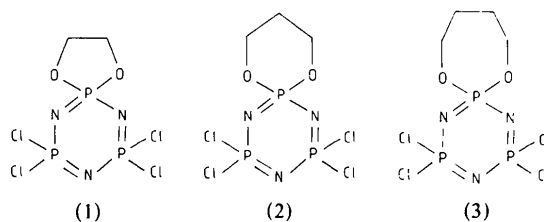
Structure determination and refinement

(1) The structure was easily solved by direct methods using *SHELX*76 (Sheldrick, 1976). All 14 non-hydrogen atoms of the asymmetric unit (the molecule has no site symmetry) were located from the best E map. After several cycles of least-squares calculations the refinement converged to $R = 5.9\%$. Hydrogen atoms were located from Fourier difference maps and refined freely giving a final R value of 5·6% and $R_w = 5.9\%$ (H atoms isotropic, others anisotropic). The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 3 and 4, and Fig. 1 shows the averaged bond lengths and angles.*

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* Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Domenicano, Vaciago & Coulson (1975a).

Table 3. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\mathrm{\AA}^2 \times 10^3)$ *for compound* (1)

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl(41)	838 (2)	2306 (2)	7390 (1)	73
Cl(42)	2561 (2)	−63 (2)	5748 (1)	82
Cl(61)	7020 (2)	7632 (2)	7369 (2)	80
Cl(62)	8087 (2)	4754 (2)	5677 (1)	93
P(2)	6289 (1)	2972 (1)	9045 (1)	43
P(4)	3309 (1)	2206 (1)	7133 (1)	45
P(6)	6548 (1)	5000 (1)	7099 (1)	46
N(1)	7398 (5)	4591 (5)	8364 (3)	53
N(3)	4193 (5)	1875 (4)	8425 (3)	54
N(5)	4449 (5)	3892 (5)	6540 (3)	54
O(21)	7297 (4)	1585 (4)	9085 (3)	62
O(22)	6486 (5)	3691 (4)	10569 (3)	65
C(21)	8325 (7)	1884 (7)	10370 (5)	66
C(22)	7332 (10)	2706 (8)	11317 (5)	75
H(211)	9626 (79)	2629 (72)	10255 (49)	80 (15)
H(212)	8418 (85)	857 (85)	10539 (56)	98 (19)
H(221)	6327 (68)	1819 (68)	11564 (44)	62 (13)
H(222)	8387 (116)	3577 (114)	11918 (75)	164 (31)

(2) The structure was solved by direct methods using *SHELX*84 (Sheldrick, 1984). One Cl and two P atoms were located from the best *E* map. Several cycles of refinement followed by a difference synthesis revealed all the 11 remaining non-hydrogen atoms.
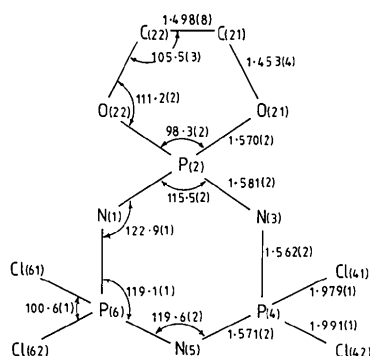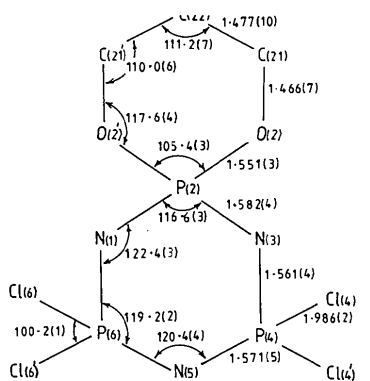

Fig. 1. Averaged molecular dimensions (Å, deg) of (1).

Fig. 2. Averaged molecular dimensions (Å, deg) of (2) (primed atoms are related by symmetry to corresponding unprimed atoms).

Table 4. *Bond lengths* (Å) *and angles* (°) *for compound* (1)

P(4)-Cl(41)	1·982 (1)	P(4)-Cl(42)	1·995 (2)
P(6)-Cl(61)	1·975 (1)	P(6)-Cl(62)	1·987 (1)
N(1)-P(2)	1·584 (3)	N(3)-P(2)	1·577 (3)
O(21)-P(2)	1·574 (3)	O(22)-P(2)	1·566 (3)
N(3)-P(4)	1·564 (3)	N(5)-P(4)	1·575 (3)
N(1)-P(6)	1·560 (3)	N(5)-P(6)	1·566 (3)
C(21)-O(21)	1·440 (5)	C(22)-O(22)	1·466 (5)
C(22)-C(21)	1·498 (8)		
H(211)-C(21)	1·001 (56)	H(221)-C(22)	0·934 (48)
H(212)-C(21)	0·894 (61)	H(222)-C(22)	0·963 (78)
N(3)-P(2)-N(1)	115·5 (2)	O(21)-P(2)-N(1)	111·6 (2)
O(21)-P(2)-N(3)	108·6 (2)	O(22)-P(2)-N(1)	109·7 (2)
O(22)-P(2)-N(3)	111·8 (2)	O(22)-P(2)-O(21)	98·3 (2)
Cl(42)-P(4)-Cl(41)	100·4 (1)	N(3)-P(4)-Cl(41)	109·3 (1)
N(3)-P(4)-Cl(42)	108·5 (1)	N(5)-P(4)-Cl(41)	108·8 (1)
N(5)-P(4)-Cl(42)	109·3 (1)	N(5)-P(4)-N(3)	118·9 (2)
Cl(62)-P(6)-Cl(61)	100·7 (1)	N(1)-P(6)-Cl(61)	109·3 (1)
N(1)-P(6)-Cl(62)	108·2 (2)	N(5)-P(6)-Cl(61)	109·0 (1)
N(5)-P(6)-Cl(62)	108·9 (1)	N(5)-P(6)-N(1)	119·2 (2)
P(6)-N(1)-P(2)	123·0 (2)	P(4)-N(3)-P(2)	122·8 (2)
P(6)-N(5)-P(4)	119·6 (2)	C(21)-O(21)-P(2)	111·4 (3)
C(22)-O(22)-P(2)	111·1 (3)	C(22)-C(21)-O(21)	105·1 (4)
C(21)-C(22)-O(22)	105·8 (4)		
H(211)-C(21)-O(21)	103·0 (29)	H(211)-C(21)-C(22)	119·2 (30)
H(212)-C(21)-O(21)	111·7 (38)	H(212)-C(21)-C(22)	114·3 (38)
H(212)-C(21)-H(211)	103·1 (46)	H(222)-C(22)-H(221)	124·8 (56)
H(221)-C(22)-O(22)	104·7 (31)	H(221)-C(22)-C(21)	112·0 (30)
H(222)-C(22)-O(22)	108·9 (49)	H(222)-C(22)-C(21)	99·4 (50)

(The molecule has a mirror plane, which passes through the plane of the 6-membered N_3P_3 ring.) The refinement converged to $R = 3.9\%$. H atoms were located from a difference map and refined freely giving a final R value of 3.3% and $R_w = 3.6\%$ (H atoms isotropic, others anisotropic). The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 5 and 6, and Fig. 2 shows the averaged molecular dimensions.

(3) The structure was solved using Patterson methods to locate two Cl atoms. Four cycles of least-squares refinement followed by a difference synthesis
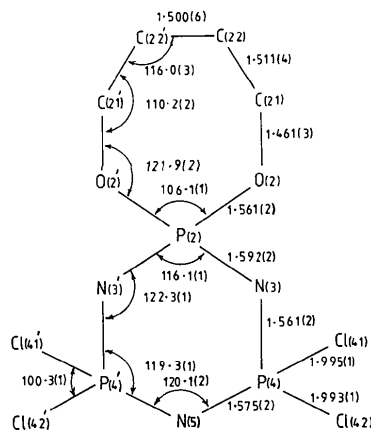

Fig. 3. Molecular dimensions (Å, deg) of (3) (primed atoms are related by symmetry to corresponding unprimed atoms).

Table 5. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for compound* (2)

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Cl(4)	1431 (2)	1587 (1)	4594 (3)	85
Cl(6)	1433 (3)	1212 (2)	10144 (3)	101
P(2)	0	3642 (1)	7740 (3)	40
P(4)	0	1983 (1)	5904 (1)	48
P(6)	0	1765 (1)	8973 (3)	56
N(1)	0	2917 (4)	9150 (7)	62
N(3)	0	3138 (4)	6123 (6)	50
N(5)	0	1295 (5)	7363 (9)	82
O(2)	1159 (4)	4332 (3)	7902 (5)	65
C(21)	1145 (8)	5275 (5)	7068 (8)	88
C(22)	0	5843 (7)	7446 (11)	114
H(211)	1224 (52)	5052 (55)	5870 (99)	78 (17)
H(212)	1735 (49)	5605 (52)	7272 (97)	74 (19)
H(221)	0	6400 (130)	7171 (311)	150 (59)
H(222)	0	6050 (100)	8403 (213)	122 (44)

Table 7. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for compound* (3)

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Cl(41)	−1408 (1)	3561 (1)	−317 (1)	60
Cl(42)	1447 (1)	3640 (1)	−114 (1)	76
P(2)	0	1375 (1)	2500	32
P(4)	41 (1)	3135 (1)	1004 (1)	38
N(3)	111 (2)	1992 (2)	1029 (2)	44
N(5)	0	3710 (2)	2500	59
O(2)	1145 (2)	687 (1)	2828 (2)	41
C(21)	1348 (3)	−189 (2)	1950 (3)	43
C(22)	699 (3)	−1059 (2)	2590 (3)	44
H(211)	1032 (32)	−83 (18)	901 (34)	50 (8)
H(212)	2345 (28)	−245 (20)	1948 (32)	45 (8)
H(221)	1076 (35)	−1624 (22)	2100 (34)	60 (9)
H(222)	966 (25)	−1165 (18)	3647 (28)	31 (6)

Table 6. *Bond lengths* (Å) *and angles* (°) *for compound* (2)

P(4)-Cl(4)	1·986 (2)	P(6)-Cl(6)	1·987 (2)
N(1)-P(2)	1·581 (6)	N(3)-P(2)	1·582 (5)
O(2)-P(2)	1·551 (3)	N(3)-P(4)	1·565 (6)
N(5)-P(4)	1·585 (7)	N(1)-P(6)	1·557 (6)
N(5)-P(6)	1·557 (7)		
C(21)-O(2)	1·466 (7)	C(22)-C(21)	1·477 (10)
H(211)-C(21)	1·103 (85)	H(212)-C(21)	0·790 (59)
H(221)-C(22)	0·787 (190)	H(222)-C(22)	0·890 (180)
Cl(4)-P(4)-Cl(4)	100·2 (2)	Cl(6)-P(6)-Cl(6)	100·3 (2)
N(3)-P(2)-N(1)	116·6 (3)	O(2)-P(2)-N(1)	107·2 (2)
O(2)-P(2)-N(3)	109·9 (2)	N(3)-P(4)-Cl(4)	109·7 (1)
N(5)-P(4)-Cl(4)	108·5 (2)	N(5)-P(4)-N(3)	118·6 (3)
N(1)-P(6)-Cl(6)	108·7 (2)	N(5)-P(6)-Cl(6)	108·9 (2)
N(5)-P(6)-N(1)	119·7 (3)		
P(6)-N(1)-P(2)	122·3 (4)	P(4)-N(3)-P(2)	122·5 (3)
P(6)-N(5)-P(4)	120·4 (4)	C(21)-O(2)-P(2)	117·6 (4)
O(2)-P(2)-O(2)	105·4 (3)	C(22)-C(21)-O(2)	110·0 (6)
C(21)-C(22)-C(21)	111·2 (7)		
H(211)-C(21)-O(2)	104·2 (40)	H(211)-C(21)-C(22)	114·9 (33)
H(212)-C(21)-O(2)	111·3 (56)	H(212)-C(21)-C(22)	108·3 (48)
H(212)-C(21)-H(211)	108·0 (68)	H(221)-C(22)-C(21)	115·0 (79)
H(222)-C(22)-C(21)	112·1 (43)	H(222)-C(22)-H(221)	89·8 (187)

Table 8. *Bond lengths* (Å) *and angles* (°) *for compound* (3)

P(4)-Cl(41)	1·995 (1)	P(4)-Cl(42)	1·993 (1)
N(3)-P(2)	1·592 (2)	O(2)-P(2)	1·561 (2)
N(3)-P(4)	1·561 (2)	N(5)-P(4)	1·575 (2)
C(21)-O(2)	1·461 (3)	C(22)-C(21)	1·511 (4)
C(22)-C(22^i)	1·500 (6)		
H(211)-C(21)	1·004 (31)	H(212)-C(21)	1·074 (30)
H(221)-C(22)	0·989 (32)	H(222)-C(22)	0·998 (25)
Cl(42)-P(4)-Cl(41)	100·3 (1)	N(3)-P(4)-Cl(41)	109·6 (1)
N(3)-P(4)-Cl(42)	108·4 (1)	N(5)-P(4)-Cl(41)	108·4 (1)
N(5)-P(4)-Cl(42)	109·2 (1)	N(5)-P(4)-N(3)	119·3 (1)
N(3)-P(2)-N(3)	116·1 (1)	O(2)-P(2)-N(3)	112·4 (1)
O(2)-P(2)-O(2)	106·1 (1)		
P(4)-N(3)-P(2)	122·3 (1)	P(4)-N(5)-P(4)	120·1 (2)
C(21)-O(2)-P(2)	121·9 (2)	C(22)-C(21)-O(2)	110·2 (2)
H(211)-C(21)-O(2)	110·5 (15)	H(211)-C(21)-C(22)	110·0 (17)
H(212)-C(21)-O(2)	103·9 (15)	H(212)-C(21)-C(22)	115·2 (15)
H(212)-C(21)-H(211)	106·8 (24)	H(221)-C(22)-C(21)	103·3 (20)
H(222)-C(22)-C(21)	111·9 (15)	H(222)-C(22)-H(221)	102·7 (24)

Symmetry code (reference atoms at x, y, z): (i) $-x$, y, $0\cdot5 - z$.

Stewart, Davidson & Simpson (1965) for the non-H and H atoms respectively.*

revealed all the remaining nine non-hydrogen atoms. (The molecule has a diad axis of symmetry along the N_5P_2 line.) The refinement converged to $R = 7 \cdot 0\%$. H atoms were located from a Fourier difference map and refined freely giving a final R value of $4 \cdot 1\%$ and $R_w = 4 \cdot 5\%$ (H atoms isotropic, others anisotropic). The positional and equivalent isotropic thermal parameters and bond lengths and angles are listed in Tables 7 and 8, and Fig. 3 shows the molecular dimensions.

The calculations were performed on a DEC VAX11/750 computer using the *SHELX*76 and *SHELX*84 program systems. Neutral-atom scattering factors were taken from Cromer & Mann (1968) and

Discussion of structures

The P–N ring bonds in cyclophosphazenes are of equal length (in a given structure) provided all the substituents, R, on the P atoms are the same (for a summary see Allcock, 1972). Mani, Ahmed & Barnes (1965, 1966) were the first to observe that when the substituents differed in electron-withdrawing power

* Lists of anisotropic thermal parameters and structural factors, and data related to least-squares-plane and dihedral-angle calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39708 (86 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 9. *A comparison of bond angles (°) in some geminal bis-substituted derivatives of hexachlorocyclotriphosphazatrienes*

	α	β	γ	δ	α'	γ'	$\alpha-\alpha'$	$\gamma-\gamma'$
(4)	118·4(2)	121·4(3)	118·4(2)	121·4(3)	101·4(7)	101·4(7)	17·0(7)	17·0(7)
(1)	115·5(2)	122·9(1)	119·1(1)	119·6(2)	98·3(2)	100·6(1)	17·2(2)	18·5(1)
(2)	116·6(3)	122·4(3)	119·2(2)	120·4(4)	105·4(3)	100·3(1)	11·2(4)	18·9(2)
(3)	116·1(1)	122·3(1)	119·3(1)	120·1(2)	106·1(1)	100·3(1)	10·0(1)	19·0(1)
(5)	115·2(2)	122·0(3)	119·7(3)	119·2(3)	104·4(3)	100·3(1)	10·8(4)	19·4(3)
(8)	111·7(4)	124·1(3)	119·2(3)	119·1(6)	104·0(5)	99·3(2)	7·6(6)	19·9(4)

the P-N ring showed significantly different P-N bond lengths in the R_2P-N-PR_2' segments. If R was more electron-supplying than R' then R_2P-N was longer, and N-PR_2' shorter than the P-N bonds in symmetric segments R_2P-N-PR_2 or R_2'P-N-PR_2'. The mean bond lengths in the asymmetric segments, however, differed little from those in the symmetric segments.

This is best demonstrated by the structure of compounds (4)-(7).

(4)   (5)

(6)   (7)
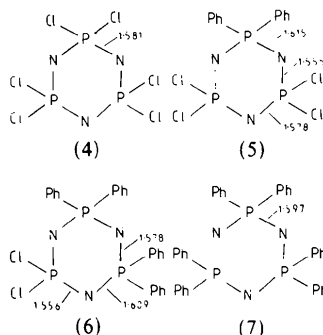
Basicity measurements have demonstrated the electron-releasing capacity of the phenyl groups (relative to the Cl atoms, which are the standard) (Feakins, Nabi, Shaw & Watson, 1968). The same type of measurements also show that acyclic alkoxy groups are of the same order or somewhat less base strengthening than phenyl groups (Feakins, Last, Neemuchwala & Shaw, 1965). No such data are to date available on alkoxy groups forming part of a spiro structure. It is known, however, that conformation does affect electron release (Shaw & Nabi, 1981), and ring structures will have more constraints than acyclic analogues in their conformational preferences. Basicity measurements probe the molecule perturbed by the proton, whilst X-ray crystallography investigates the unperturbed molecule. Ingold (1953) has drawn attention to the fact that electronic effects could be divided into those present in the ground state, and those called into being at the demand of a reagent. All three compounds reported here show a longer P-N bond adjacent to the P atom carrying the alkanedioxy group.

If we compare the difference, Δ(P-N),* in the two bonds in question, *viz* R_2P-N and N-PCl$_2$ ($R =$

substituent other than Cl), and compare these with those observed in compound (5) and in the geminal bis(*tert*-butylamino) derivative, $N_3P_3(NHBu')_2Cl_4$ (8) (Begley, Sowerby & Bamgboye, 1979), we obtain the following values: (1) 0·019 (3), (2) 0·021 (7), (3) 0·031 (3), (5) 0·060 (7) and (8) 0·055 (7) Å. Alkylamino groups are very much more base-strengthening than phenyl or alkoxy groups (Feakins, Last & Shaw, 1964; Feakins, Last, Neemuchwala & Shaw, 1965; Feakins, Last, Nabi & Shaw, 1966). The general trend between Δ(P-N) and basicity is in the right direction, except for the inverted order of (5) and (8), the latter having, however, rather high e.s.d.'s.

Following earlier observations (Bailey & Prout, 1965; Carter, McPhail & Sim, 1966; Nygaard, Bojesen, Pedersen & Rastrup-Andersen, 1968) on the distortions of substituted benzene rings, especially by nitro groups, Domenicano, Vaciago & Coulson (1975*a*, *b*), Domenicano, Mazzeo & Vaciago (1976), Domenicano & Vaciago (1979) and Domenicano & Murray-Rust (1979) drew attention to the fact that in benzene rings changes in bond angles are more reliable guides to electronic shifts than are changes in bond lengths. We compare the bond angles in compounds (1)-(5) and (8) (using Fig. 4, Bullen, 1971) in Table 9.

As in benzene rings, the changes are most pronounced in the cyclotriphosphazatriene ring in the angles nearest the substituent, *viz* α and β, the former decreasing, the latter increasing, with increasing electron supply of the substituents relative to (4). Whilst the $\gamma-\gamma'$ values remain largely unchanged, the $\alpha-\alpha'$ values vary considerably and appear to decrease with increasing electron supply to the ring.

In general, inductive effects increase with increased α branching of alkyl groups. The basicities of hexa-alkoxycyclotriphosphazatrienes, $N_3P_3(OR)_6$, increase in the order $R = Me < Et < Pr^i$, the $pK_{a,1}'$ values being $-1·9$, $-0·2$ and $1·4$ respectively (Feakins,

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*Errors are calculated using the formula given by Mosteller, Rourke & Thomas (1970).
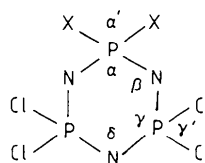
Fig. 4. Generalized bond-angle diagram of geminal bis-substituted tetrachlorocyclotriphosphazatrienes, $N_3P_3X_2Cl_4$.

Last, Neemuchwala & Shaw, 1965). A very slight trend in a similar direction can be discerned for the geminal derivatives, $N_3P_3Cl_2(NHR)_4$ ($R = Et$, Pr^i, Bu^t) (Feakins, Last, Nabi & Shaw, 1966). The ^{31}P chemical shifts of these last four compounds show significant upfield trends with increased α branching (Keat, Shaw & Woods, 1976; Parkes & Shaw, 1984). Thus, measurements on unperturbed and perturbed states point in the same general direction.

If we make the working hypothesis that in *closely related structures*, e.g. in alkoxyphosphazenes, increased electron supply from substituents causes an upfield shift in the δ value of the substituted cyclotriphosphazatriene ^{31}P nucleus, then we could argue that in compounds (1)–(3) the dioxyalkane residue supplies most electrons (relative to atoms) in compound (2) and least in compound (1), i.e. we have an electron-releasing effect (2) > (3) > (1). Examination of the O–P bonds in these three compounds shows that such a trend can just about be discerned with the O–P bond being the shortest in compound (2) and the longest in compound (1).

However, no such differential trend is observable in the ring P–N bonds, Δ(P–N) showing no statistically significant trends. In compound (1) one P–Cl bond length in each PCl_2 unit is significantly longer than the other, the two long bonds being in a *cis* relationship. Such non-equivalence has been observed previously, e.g. in $N_3P_3Ph_2Cl_4$ (Mani, Ahmed & Barnes, 1965), in $N_3P_3Ph_4Cl_2$ (Mani, Ahmed & Barnes, 1966) and in $N_3P_3(NPPh_3)_2Cl_4$ (Krishnaiah, Ramamurthy, Ramabrahmam & Manohar, 1981). Such non-equivalence should be readily discernible by ^{35}Cl NQR spectroscopy, longer P–Cl bonds being associated with lower ^{35}Cl NQR frequencies (Keat, Porte, Tong & Shaw, 1972; Dalgleish, Keat, Porte, Tong, Hasan & Shaw, 1975; Dalgleish, Keat, Porte & Shaw, 1977).

The similarity of the bond lengths of the cyclotriphosphazatriene rings in the three monospiro compounds reported here is mirrored by the bond angles in their N_3P_3 rings, which again show no statistically significant differences. In the phosphate rings, however, the angles COP and OPO increase significantly with ring size. Interestingly whilst the OPO angles vary from 98·3 (2) (1) to 105·4 (3) (2) and 106·1 (1)° (3), the corresponding endocyclic NPN angles are virtually constant at 116·1 (6)°. In most phosphazene structures studied so far, widening of the *exo* angle produced a narrowing of the *endo* angle and *vice versa* (Ahmed, Singh & Barnes, 1969).

On present evidence the structural differences between compounds (1)–(3) seem to be confined to the phosphate rings and do not appear to affect significantly the cyclotriphosphazatriene rings, although we shall demonstrate shortly that generally these rings are very sensitive to changes in the electron supply of the substituents.

The OPO angle of 98·3 (2)° in compound (1) is near the upper end of the range (95·4–98·5°) described by Wieczorek (1980) for this structural type. That of compound (2) at 105·4 (3)° is unremarkable.

Few structural studies have been reported on 7-membered phosphate rings. Our value of 106·1 (1)° for the OPO angle is in excellent agreement with that of Coulter (1975) for tetramethylenephosphoric acid (106·8°) and somewhat smaller than that reported by Kung, Marsh & Kainosho (1977) for 2′,5′-arabinosyl-cytidine monophosphate (109·4°), the latter being a fused bicyclic system.

The POC angles increase considerably [111·2 (2) for (1), 117·6 (4) for (2), 121·9 (2)° for (3)] with increasing ring size. Those of compound (1) fall well in the range (106·8–114·4°) described (Wieczorek, 1980) for seventeen 1,3,2-dioxaphospholane rings. That of compound (2) at 117·6° is unexceptional (Warrent, Caughlan, Hargis, Yee & Bentrude, 1978). The same angle in compound (3) of 121·9° again closely resembles those in tetramethylenephosphoric acid (121·5 and 121·7°), and is smaller than those in the cyclic nucleotide (127·2 and 124·0°).

In compound (1) the OPO plane is twisted relative to the perpendicular of the NPN plane (of the P atom common to both) by 2°; no such twist is observed for compound (2), but compound (3) has a twist of 8°. On the other hand, whilst neither compound (1) nor (3) shows any bending of the above plane, the OPO plane of compound (2) is bent by 3° away from N(3), the side towards which the C atoms C(21) and C(21′) of the chair protrude.

Conformation

Numerous structural investigations have been carried out on cyclic phosphates and related compounds. Simplified, these structures can be portrayed as in Fig. 5.

It can be seen that in all of these the environment above and below the cyclic phosphate group is different, e.g. a lone pair of electrons, a phosphoryl or thiophosphoryl linkage on one side, and another 'formally' singly bonded substituent on the other. The different environments on opposite sides of these phosphate rings are liable to affect their conformations. The phosphazene moieties of the three structures reported here provide unique examples of symmetric environments on both sides of the phosphate rings and thus should allow the phosphate rings to adopt their preferred conformations without being influenced by an unequal environment on the two
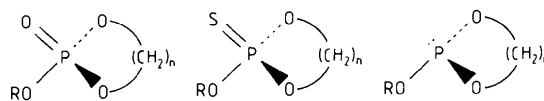

Fig. 5. Generalized diagram of monocyclic phosphate, thiophosphate and phospite.

Table 10. POCH *dihedral angles* (°) *for compounds* .(1)-(3) (*e.s.d.'s* ~3°)

Compound (1)		Compound (2)		Compound (3)	
P(2)O(21)C(21)H(211)	−98·2	P(2)O(2)C(21)H(211)	−69·3	P(2)O(2)C(21)H(211)	32·6
P(2)O(21)C(21)H(212)	151·8	P(2)O(2)C(21)H(212)	174·5	P(2)O(2)C(21)H(212)	146·8
P(2)O(22)C(22)H(221) ,̇	−97·8				
P(2)O(22)C(22)H(222)	126·6*				

* High temperature factor for H(222).

sides of these rings. In principle similar equal environ-
ments would exist in phosphate rings in suitable
quasi-phosphonium structures, $R_2P[O(CH_2)_nO]^+$.
However, because of their instability, none have so
far been isolated (Hudson, 1983*a*, *b*), although
$Me_2P[(OCH_2)_2CMe_2]^+.BF_4^-$ has been reported in sol-
ution (White, 1971).

The three cyclotriphosphazatriene rings reported
here are essentially planar (maximum deviation
0·03 Å) (Fig. 6) (Davies, 1983). In compound (1) the
five-membered phosphate ring adopts a twist-boat
non-planar conformation (Fig. 7), the two C atoms
deviating equally, but in opposite directions, from
the OPO plane. The phosphate ring in structure (2)
adopts the usual chair conformation (Fig. 8) (Clardy,
Mosbo & Verkade, 1974; Warrent, Caughlan, Hargis,
Yee & Bentrude, 1978). The conformation of the
phosphate ring in structure (3) is unusual. The C
atoms C(21) and C(21′) deviate equally and in
opposite directions from the plane defined by OPO
and the other two C atoms, C(22) and C(22′) (Fig.

9). The dihedral angles POCH of compounds (1)-(3)
are given in Table 10.

We have, however, refrained from relating $^3J(PH)$
in solution to the dihedral POCH angles in the crystals
in view of the so far not understood effect of how
changes in POC angle affect these coupling constants.
Attention to this has been drawn in POCH (Kung,
Marsh & Kainosho, 1977) and to the PSC angle in
PSCH systems (Martin & Robert, 1981).

Relationship between OPO bond angles in PO_2N_2 tetrahedra and ^{31}P chemical shifts

The three structures reported here allow a comparison
of bond lengths, bond angles, conformations and
other parameters amongst 5-, 6-, and 7-membered
spiro rings (attached in each case to a 6-membered
tetrachlorocyclotriphosphazatriene ring). A com-
parison with an acyclic analogue is not possible, as
to date no such derivative has been isolated, the
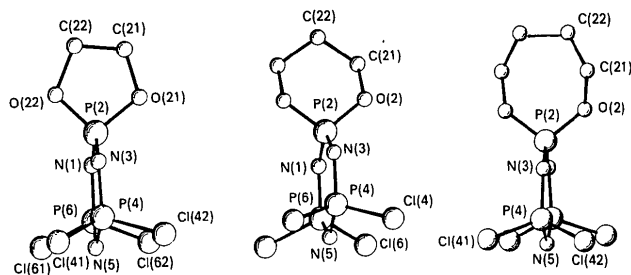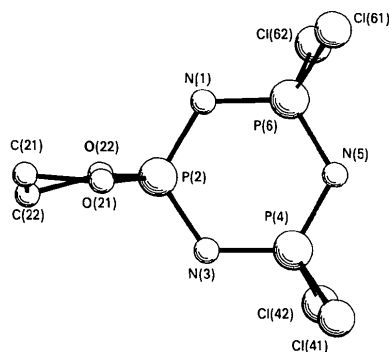preferred replacement pattern of Cl atoms by alkoxy

Fig. 6. Molecular diagrams of (1), (2) and (3) with side views of
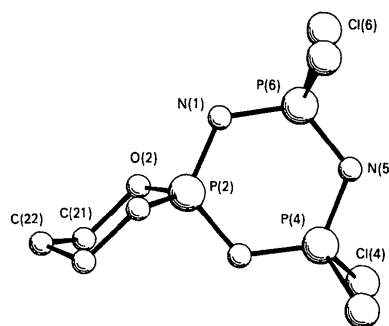N_3P_3 rings.

Fig. 8. Molecular diagram of (2) showing the conformation of the
phosphate ring.

Fig. 7. Molecular diagram of (1) showing the conformation of the
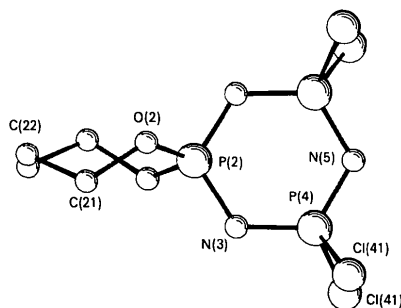phosphate ring.

Fig. 9. Molecular diagram of (3) showing the conformation of the
phosphate ring.

groups in hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, being nongeminal (Dell, Fitzsimmons & Shaw, 1966; Finer, Harris, Bond, Keat & Shaw, 1970; Schmutz & Allcock, 1975; Ramachandran & Allen, 1983). In this, the alkoxyphosphazenes differ from their amino analogues, where geminal acyclic bis(amino) derivatives, $N_3P_3Cl_4Y_2$ ($Y = NH_2$, NHMe, NHPr^i, NHBu^t, NHPh, NHCH$_2$Ph, NMe$_2$, NC$_4$H$_8$, NC$_2$H$_4$), have been isolated and characterized (Shaw, 1976; Lingley, Shaw, Woods & Krishnamurthy, 1978).

Similar variations of ^{31}P chemical shifts with ring size, as described in this paper, have been observed by Martin & Robert (1981) in the 2-oxo- and 2-thioxo-2-R-1,3,2-dithiaphospha ring systems, where 5-, 6-, 8-, 12- and 16-membered rings were studied. Large upfield shifts were observed on going from 5- to 6-membered rings, and smaller downfield shifts from 6-membered to 8-membered rings, the latter resembling acyclic analogues.

In our studies a large upfield ^{31}P chemical shift has been observed for the P(spiro) nucleus on passing from compound (1) (5-membered) to (2) (6-membered), followed by a smaller downfield shift to (3) (7-membered). We have reason to believe that the latter resembles related acyclic compounds by analogy with the cyclotriphosphazatriene system containing primary amino substituents (Parkes & Shaw, 1984).

Further support for this supposition comes from the work of Blackburn, Cohen & Todd (1964) and Blackburn, Cohen & Weatherall (1971), who noted the similarity in shift between a 7-membered ring phosphate, $(PhO)(O)P[O(CH_2)_4O]$, $\delta = 3 \cdot 7$, and its acyclic analogue, $(PhO)(O)P(OBu^n)_2$, $\delta \approx 4$. These workers noted that, in general, derivatives of quinquevalent mononuclear phosphorus oxy acids showed an upfield shift of about 16 p.p.m. from 5-membered ring structures to their acyclic analogues, whilst the latter showed a downfield shift of approximately 8 p.p.m. compared with the analogous 6-membered ring structures. Some variations in these values were noted between individual groups of compounds. None, however, contained the PO_2N_2 tetrahedra described here, where the changes are $-19 \cdot 9$ [(1) to (2)] and $+7 \cdot 0$ p.p.m. [(2) to (3)]. Gorenstein (1975) deduced an empirical correlation between ^{31}P chemical shifts and OPO bond angles for phosphate esters, noting that this need not apply to other classes of phosphoryl compounds. In his plot ^{31}P chemical-shift changes are quite large for relatively small changes in bond angles. Our data, being based on PO_2N_2 rather than on PO_4 tetrahedra, not unexpectedly do not fit his curve.

However, the values of the OPO bond angles of compounds (1)–(3), together with those from related structures (published and unpublished), allow another curve to be plotted. This, together with that

of Gorenstein (1975) [slightly modified by the deletion of aryl and acetoinediol phosphates, and by the addition (thanks to the courtesy of Dr Wechter, The Upjohn Company, who provided the sample for ^{31}P chemical-shift measurements) of a useful point (due to 2',5'-arabinosylcytidine cyclic monophosphate) to that part of the curve which slopes upwards again at angles $> 106°$], and that for SPS angles in PS$_3$C tetrahedra from Martin & Robert (1981), is displayed in Fig. 10.

The SPS curve is based on four points. Gorenstein's modified curve deduced from 12 points and ours based on 10 points both show some scatter. Two major observations emerge from Fig. 10: (i) relatively small changes in bond angles give rise to large changes in ^{31}P chemical shifts, and (ii) whilst the three curves
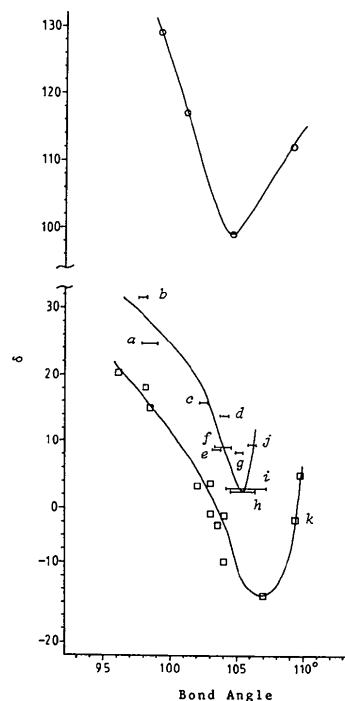

Fig. 10. Relationship between ^{31}P chemical shifts and OPO bond angles in PO$_2$N$_2$ tetrahedra (middle curve). Comparison with OPO and SPS bond angles in PO$_4$ (bottom curve) and PS$_3$C (top curve) tetrahedra respectively. (i) refers to crystal structure (error bars represent 6 e.s.d.'s), (ii) refers to ^{31}P chemical shift (repeatability $\leq \pm 0 \cdot 2$ p.p.m.). (a) N$_3$P$_3$[O(CH$_2$)$_2$O]Cl$_4$, (h) N$_3$P$_3$[O(CH$_2$)$_3$O]Cl$_4$, (j) N$_3$P$_3$[O(CH$_2$)$_4$O]Cl$_4$, (i), (ii) (this paper); (b) N$_3$P$_3$[O(CH$_2$)$_2$O]$_2$Cl$_2$, (i), (ii) (Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1984); (c) N$_3$P$_3$[O(CH$_2$)$_3$O](pyr)$_4$, (e) N$_3$P$_3$[O(CH$_2$)$_3$O](pyr)$_2$Cl$_2$ (pyr = pyrrolidino), (i), (ii) (Contractor, Hursthouse, Shaw & Shaw, 1984); (d) N$_3$HP$_3$Ph$_2$(OMe)$_3$(O), (i), (ii) (Dhathathreyan, Krishnamurthy, Vasudeva Murthy, Cameron, Chan, Shaw & Woods, 1980; Cameron, 1984); (f) spiro-ansa N$_3$P$_3$[O(CH$_2$)$_3$O]$_2$Cl$_2$, (g) dispiro N$_3$P$_3$[O(CH$_2$)$_3$O]$_2$Cl$_2$, (i), (ii) (Contractor, Hursthouse, Parkes, Shaw, Shaw & Yılmaz, 1984); (i) N$_4$P$_4$(OMe)$_8$, (i) (Ansell & Bullen, 1971), (ii) (Dhathathreyan, Krishnamurthy, Vasudeva Murthy, Shaw & Woods, 1982); (k) 2',5'-arabinosylcytidine cyclic monophosphate, (i) (Kung, Marsh & Kainosho, 1977), (ii) (this paper).

show considerable displacements in chemical shifts relative to one another, their minima, coinciding with maximum shielding, occur over a small range of bond angles, *viz* $105 \cdot 5 \pm 1 \cdot 5°$. We wish to stress that the accuracy of such curves will be greatest if the examples are taken from closely related structures (all three curves relate to alkyl derivatives), and that the curves may well need modification as more data become available. We have shown elsewhere that good agreement between P-Cl bond lengths and ^{35}Cl NQR frequencies is only obtained if a limited range of structural types are compared; thus
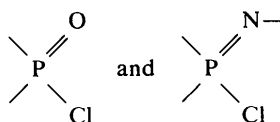
moieties give rise to lines with different slopes (Keat, Porte, Tong & Shaw, 1972; Dalgleish, Keat, Porte & Shaw, 1977; Shaw, 1977). Attempts to generalize this relationship to all P-Cl bonds gave rise to a line with large scatter (Belskii, Naumov & Nuretdinov, 1974).

Our own structural data suggest that whilst in the ground state the spiro dioxyalkane groups (1)-(3) supply electron density relative to two Cl atoms (4), bond angles and bond lengths in the cyclotriphosphazatriene rings indicate no differential electron release between the three structures (1)-(3) in the unperturbed state. The changes appear to be entirely confined to the phosphate ring with major changes in OPO and COP bond angles, and minor changes in P-O bond lengths. The ^{31}P chemical shifts of 7-membered-ring derivatives appear to resemble those of acyclic analogues.

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Temperature-Dependence Studies of α-Oxalic Acid Dihydrate

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Abstract

Single-crystal X-ray analyses were made on oxalic acid dihydrate at five different temperatures – 300, 225, 170, 130, 100 K. A few selected peak profiles at various 2θ angles were monitored; the net intensities of the reflections increase on lowering the temperature as expected and this increase is more prominent for high-2θ-angle reflections than for low ones. The cell parameters contract anisotropically on lowering the temperature in the range studied [at 300 K: $a = 6\cdot120(2)$, $b = 3\cdot6058(8)$, $c = 12\cdot057(3)$ Å, $\beta = 106\cdot29(2)°$]. The atomic thermal vibrational amplitudes decrease with decreasing temperature. The deformation density maps were investigated at 100 K: there are bonding electron densities at the midpoints of bonds C–C and C–O, as expected; the lone-pair densities around the O atoms are revealed; the hydrogen bond between the oxalic acid molecule and the water molecule is interestingly demonstrated.

Introduction

The crystal structure of oxalic acid dihydrate was first studied by Ahmed & Cruickshank (1953). The charge density study of oxalic acid dihydrate at room tem-

perature was then carried out by Coppens, Sabine, Delaplane & Ibers (1969). Recently, there have been several density studies at low temperature, *e.g.* Stevens & Coppens (1980), Dam, Harkema & Feil (1983), as a result of a common project on the density study of oxalic acid dihydrate at 100 K sponsored by the Commission on Charge, Spin and Momentum Densities of the International Union of Crystallography. The detailed comparison of the project was given in the report of Coppens *et al.* (1984). The present work presents the temperature dependence of the parameters in addition to the deformation density study at 100 K.

Experimental

A 0·34 mm diameter spherical oxalic acid crystal was cooled in a 5 mm diameter jet of cold nitrogen (from boiling liquid nitrogen); temperature of the jet adjusted from 95 K to room temperature by a heating resistor in the delivery arm; temperature of the crystal calibrated using a thermocouple with the tip at the crystal position. Intensities of the same unique set of reflections were collected with graphite-monochromated Mo $K\alpha$ radiation up to $2\theta = 90°$, except for the room-temperature ones which were collected up to 60° but with the whole sphere (four equivalent sets, total 2855 reflections). At 100 K, the additional $1\frac{1}{2}$ sets

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