

Structural Investigations of Phosphorus–Nitrogen Compounds. 3.* The Structures of $N_3P_3[O(CH_2)_3O](NC_4H_8)_4$ and *trans*- $N_3P_3[O(CH_2)_3O](NC_4H_8)_2Cl_2$ and a Comparison with $N_3P_3[O(CH_2)_3O]Cl_4$. The Effect of Replacing the Electron-Withdrawing Chlorine Atoms by Electron-Releasing Pyrrolidino Groups. P–O Bond Lengths and their Relationship to Spin–Spin Coupling Constants, $^3J(POCC)^\dagger$

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Abstract

The crystal structures of 2,2-(1',3'-propanedioxy)-4,4,6,6-tetra(pyrrolidino)cyclotriphosphazatriene, $N_3P_3[O(CH_2)_3O](NC_4H_8)_4$ (5) and 2,2-(1',3'-propanedioxy)-*trans*-4,6-dichloro-4,6-di(pyrrolidino)cyclotriphosphazatriene, $N_3P_3[O(CH_2)_3O](NC_4H_8)_2Cl_2$ (4) were determined at 295 (2) K and compared with that of 2,2-(1',3'-propanedioxy)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3[O(CH_2)_3O]Cl_4$ (2). [Crystal data: (4): orthorhombic, $P2_12_12_1$, $a = 9.344$ (2), $b = 14.505$ (3), $c = 27.979$ (5) Å, $V = 3792.5$ (1.0) Å³, $Z = 8$, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 5.45$ cm⁻¹; (5): triclinic, $P\bar{1}$, $a = 10.439$ (7), $b = 15.708$ (7), $c = 17.329$ (8) Å, $\alpha = 114.74$ (4), $\beta = 79.21$ (5), $\gamma = 99.32$ (5)°, $V = 2524.1$ (2.2) Å³, $Z = 4$, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 2.20$ cm⁻¹.] Full-matrix least-squares refinements led to R values of 4.4% for (4), and 5.9% for (5) using 3106 and 6640 unique reflections respectively [$F_o > 3\sigma(F_o)$]. The effects of replacing the electron-withdrawing Cl atoms by the electron-releasing

pyrrolidino groups on the structural parameters are noted. With increasing electron supply the P–O bond lengthens and the three-bond spin–spin coupling constant, $^3J(POCC)$, decreases.

Introduction

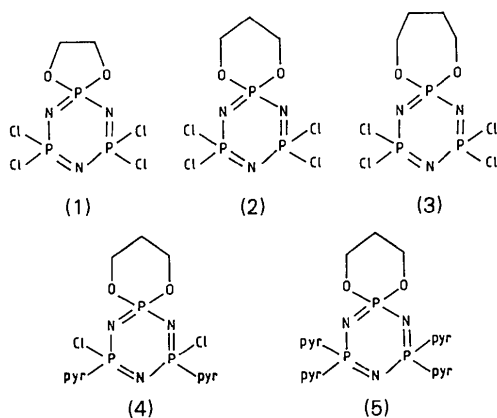
In Part 1 (Contractor, Hursthouse, Shaw, Shaw & Yilmaz, 1985) of this series we compared the crystal and molecular structures of 2,2-(1',2'-ethanedioxy)-, $N_3P_3[O(CH_2)_2O]Cl_4$, (1), 2,2-(1',3'-propanedioxy)-, $N_3P_3[O(CH_2)_3O]Cl_4$, (2) and 2,2-(1',4'-butanedioxy)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3[O(CH_2)_4O]Cl_4$ (3). In these three compounds we kept one part of the spiro compound, namely the cyclotriphosphazatriene moiety, constant and varied the phosphate ring. In the present paper we keep the six-membered phosphate ring constant and vary the electron-donating power of the phosphazene ring. We report here the structure of 2,2-(1',3'-propanedioxy)-4,4,6,6-tetra(pyrrolidino)-, $N_3P_3[O(CH_2)_3O]pyr_4$ (pyr = pyrrolidino), (5) and 2,2-(1',3'-propanedioxy)-*trans*-4,6-dichloro-4,6-di(pyrrolidino)cyclotriphosphazatriene, $N_3P_3[O(CH_2)_3O]pyr_2Cl_2$, (4), and compare them with that of 2,2-(1',3'-propanedioxy)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3[O(CH_2)_3O]Cl_4$, (2). The preparation and NMR

* Part 2: Fincham, Hursthouse, Parkes, Shaw & Shaw (1986).

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spectroscopic properties [except $^3J(\text{POCC})$] are described elsewhere (Alkubaisi, Parkes & Shaw, 1987).



The pyrrolidino group is the most electron-donating secondary amino group we have observed in our basicity studies on cyclophosphazenes and we have obtained values of 5.9 and 3.0 for α_{pyr} and γ_{pyr} respectively (Shaw & Nabi, 1981; Gündüz, Kılıç & Shaw, 1987). Whilst these studies measure the electron density (perturbed under the influence of a proton) at a ring N atom of the cyclophosphazatriene ring, X-ray crystallography measures parameters of the unperturbed molecule. Nevertheless, a fairly close relationship has been noted between the effects observed by the two types of measurements.

The exceptional tellurium basicity of tri(pyrrolidino)phosphine, pyr_3P , has been reported (Rømming, Iversen & Songstad, 1980). It has also been noted that tri(pyrrolidino)phosphine oxide is the most electron-donating of all aprotic solvents, and the best complexing agent of all phosphoryl compounds, $\text{R}_3\text{P}=\text{O}$, towards hard metal cations (Ozari & Jagur-Grodzinski, 1974). The crystal structures of two mononuclear phosphorus derivatives, tri(pyrrolidino)phosphine selenide, pyr_3PSe , and the analogous telluride, pyr_3PTe , have been described (Rømming, Maartmann-Moe & Songstad, 1984). The structure of octa(pyrrolidino)cyclophosphazetetraene, $\text{N}_4\text{P}_4\text{pyr}_8$, has also been reported (Bovin, Labarre & Galy, 1979).

The electron-releasing capacity $\text{pyr} > \text{NMe}_2 > \text{pip} > \text{morph}$ (where pip = piperidino, morph = morpholino) has been established for uncharged π -systems in the ground state, as well as for aminobenzene/trinitrobenzene charge-transfer complexes (Effenberger, Fischer, Schoeller & Stohrer, 1978) and for enamines (Hickmott, 1982).

We wished to investigate the changes caused by replacing the four Cl atoms in compound (2) by, respectively, two (4) and four (5) pyrrolidino groups. We had deduced earlier (Contractor, Hursthouse, Parkes, Shaw, Shaw & Yilmaz, 1983) from the intrinsic asymmetry of the OCH_2 and CH_2 protons of the

Table 1. Additional crystal data and experimental information

	(4)	(5)
M_r	420.12	489.48
D_m (g cm^{-3})	1.471	1.288
D_x (g cm^{-3})	1.490	1.294
Crystal size (mm)	$0.50 \times 0.25 \times 0.25$	$0.40 \times 0.20 \times 0.25$
Total unique data	3757	8864
Max. Δ/σ in final LS cycle	0.08	0.19
Least-squares parameters	421	575
$(\Delta\rho)_{\text{max}}$ (e \AA^{-3})	≤ 0.4	≤ 0.9
Weights	$[\sigma^2(F_o) + 0.002F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0003F_o^2]^{-1}$
Max. h, k, l	11, 17, 33	$\pm 12, \pm 18, 20$

1,3-dioxypropane group, as observed in the ^1H NMR spectrum of the dipyrrolidino derivative (4), that the amino groups had a *trans* disposition and we wished, in addition, to confirm crystallographically these deductions based on NMR spectroscopy.

We had observed earlier (Deutsch, Hursthouse, Kılıç, Parkes, Shaw & Shaw, 1987) that changes in P–NAlk bond length and the stereochemistry of the N atom affected three-bond spin–spin coupling constants, $^3J(\text{PNCC})$. We intended to investigate analogous changes in P–O bond lengths and $^3J(\text{POCC})$ coupling constants.

Experimental

Crystals were grown as follows: (4) from methylene chloride, m.p. 452–453 K, (5) from ethyl acetate, m.p. 412–413 K. Both crystals were colourless and block-shaped. The flotation method was used to measure the densities. Unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections [$16 < \theta(\text{Mo K}\alpha) < 17^\circ$] automatically centred on an Enraf–Nonius CAD-4 diffractometer. The intensity data were recorded on the same instrument at 295 (2) K, using graphite-monochromatized radiation in the $\omega/2\theta$ scan mode, in a manner previously described in detail by Hursthouse, Jones, Malik & Wilkinson (1979), with θ ranges of 2–25° and 1.5–25° for (4) and (5) respectively. The data for all the compounds were corrected for Lorentz and polarization effects; no absorption corrections. Additional crystal data and experimental information is given in Table 1. ^{13}C NMR spectra were recorded in deuteriochloroform on a Jeol FX200 NMR spectrometer operating at 50.1 MHz.

Structure determination and refinement

The structures were solved by direct methods using *SHELX76* (Sheldrick, 1976).

(4) The first *E* map revealed 15 non-H atoms out of 46 of the asymmetric unit (two independent molecules). The *R* value at this stage was 39%. Several cycles of refinement, followed by a difference synthesis, revealed all the remaining 31 non-H atoms. Although

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

$$U_{eq} = \frac{1}{3} \sum_i U_{ii}$$

	x	y	z	U_{eq}
Cl(4A)	5299 (3)	4630 (1)	-358 (1)	88
Cl(6A)	-669 (2)	5570 (2)	-154 (1)	85
P(6A)	1172 (2)	4843 (1)	-21 (1)	50
P(4A)	3841 (2)	5575 (1)	-96 (1)	44
P(2A)	2800 (1)	5103 (1)	787 (1)	37
N(1A)	1339 (5)	4829 (4)	532 (2)	57
N(3A)	4014 (5)	5518 (4)	462 (2)	50
N(5A)	2354 (6)	5345 (4)	-333 (2)	64
N(41A)	4408 (5)	6561 (3)	-288 (2)	51
N(61A)	833 (6)	3827 (4)	-225 (2)	61
O(21A)	3455 (4)	4251 (3)	1058 (2)	53
O(22A)	2493 (4)	5809 (2)	1198 (1)	46
C(21A)	2691 (8)	3906 (4)	1472 (3)	63
C(22A)	1668 (7)	5467 (4)	1606 (2)	52
C(23A)	2447 (7)	4664 (4)	1824 (2)	58
C(61A)	765 (11)	3655 (6)	-748 (3)	98
C(63A)	-316 (15)	2925 (7)	-802 (4)	127
C(65A)	-778 (18)	2628 (10)	-335 (5)	167
C(67A)	-107 (10)	3188 (5)	38 (3)	90
C(41A)	5810 (7)	6919 (5)	-123 (2)	65
C(43A)	6487 (9)	7280 (7)	-566 (3)	96
C(45A)	5338 (10)	7489 (7)	-906 (3)	98
C(47A)	4125 (8)	6851 (5)	-787 (3)	75
Cl(6B)	864 (2)	2607 (1)	2707 (1)	81
Cl(4B)	-4967 (3)	1687 (2)	2167 (1)	91
P(6B)	-653 (2)	2315 (1)	2194 (1)	53
P(4B)	-3476 (2)	2660 (1)	2365 (1)	52
P(2B)	-1998 (2)	3714 (1)	1712 (1)	48
N(5B)	-2064 (6)	2092 (4)	2480 (2)	72
N(3B)	-3455 (5)	3388 (4)	1951 (2)	59
N(1B)	-613 (6)	3167 (4)	1846 (2)	67
N(61B)	-50 (6)	1397 (4)	1934 (2)	60
N(41B)	-4117 (5)	3100 (4)	2844 (2)	58
O(22B)	-2137 (5)	3723 (3)	1154 (2)	62
O(21B)	-1721 (5)	4757 (3)	1840 (2)	64
C(22B)	-3034 (7)	4430 (6)	933 (3)	70
C(23B)	-2616 (8)	5372 (5)	1094 (3)	84
C(21B)	-2674 (9)	5429 (5)	1623 (3)	83
C(61B)	1195 (9)	1443 (5)	1604 (3)	80
C(63B)	1784 (10)	481 (6)	1613 (4)	100
C(65B)	819 (21)	-74 (7)	1846 (5)	193
C(67B)	-167 (11)	482 (5)	2146 (3)	87
C(41B)	-5276 (9)	3783 (6)	2846 (3)	78
C(43B)	-5684 (14)	3856 (9)	3360 (4)	123
C(45B)	-5276 (15)	3018 (9)	3581 (4)	145
C(47B)	-4150 (10)	2565 (6)	3298 (3)	85

Table 3. Bond lengths (\AA) and bond angles ($^\circ$) for compound (4)

P(4A)-Cl(4A)	2.067 (2)	P(6A)-Cl(6A)	2.052 (3)
N(1A)-P(6A)	1.554 (5)	N(5A)-P(6A)	1.584 (5)
N(61A)-P(6A)	1.612 (5)	N(3A)-P(4A)	1.572 (4)
N(5A)-P(4A)	1.574 (5)	N(41A)-P(4A)	1.616 (5)
N(1A)-P(2A)	1.592 (5)	N(3A)-P(2A)	1.574 (4)
O(21A)-P(2A)	1.575 (4)	O(22A)-P(2A)	1.565 (4)
C(41A)-N(41A)	1.483 (8)	C(47A)-N(41A)	1.484 (8)
C(61A)-N(61A)	1.484 (8)	C(67A)-N(61A)	1.473 (9)
C(21A)-O(21A)	1.448 (7)	C(22A)-O(22A)	1.466 (7)
C(23A)-C(21A)	1.494 (9)	C(23A)-C(22A)	1.502 (8)
C(63A)-C(61A)	1.472 (12)	C(65A)-C(63A)	1.441 (15)
C(67A)-C(65A)	1.464 (13)	C(43A)-C(41A)	1.487 (10)
C(45A)-C(43A)	1.465 (10)	C(47A)-C(45A)	1.500 (10)
P(6B)-Cl(6B)	2.062 (2)	P(4B)-Cl(4B)	2.059 (3)
N(5B)-P(6B)	1.575 (5)	N(1B)-P(6B)	1.573 (5)
N(61B)-P(6B)	1.619 (6)	N(5B)-P(4B)	1.588 (5)
N(3B)-P(4B)	1.568 (5)	N(41B)-P(4B)	1.601 (6)
N(3B)-P(2B)	1.589 (5)	N(1B)-P(2B)	1.564 (5)
O(22B)-P(2B)	1.566 (4)	O(21B)-P(2B)	1.576 (5)
C(61B)-N(61B)	1.487 (8)	C(67B)-N(61B)	1.458 (8)
C(41B)-N(41B)	1.468 (9)	C(47B)-N(41B)	1.487 (8)
C(22B)-O(22B)	1.462 (8)	C(21B)-O(21B)	1.453 (8)
C(23B)-C(22B)	1.492 (11)	C(21B)-C(23B)	1.484 (12)
C(63B)-C(61B)	1.500 (11)	C(65B)-C(63B)	1.374 (14)
C(67B)-C(65B)	1.484 (13)	C(43B)-C(41B)	1.493 (11)
C(45B)-C(43B)	1.415 (14)	C(47B)-C(45B)	1.473 (13)
N(1A)-P(6A)-Cl(6A)	105.8 (2)	N(5A)-P(6A)-Cl(6A)	104.3 (2)
N(5A)-P(6A)-N(1A)	118.9 (3)	N(61A)-P(6A)-Cl(6A)	103.9 (2)
N(61A)-P(6A)-N(1A)	111.1 (3)	N(61A)-P(6A)-N(5A)	111.2 (3)
N(3A)-P(4A)-Cl(4A)	104.4 (2)	N(5A)-P(4A)-Cl(4A)	107.1 (2)
N(5A)-P(4A)-N(3A)	119.8 (3)	N(41A)-P(4A)-Cl(4A)	104.7 (2)
N(41A)-P(4A)-N(3A)	110.0 (3)	N(41A)-P(4A)-N(5A)	109.7 (3)
N(3A)-P(2A)-N(1A)	117.0 (2)	O(21A)-P(2A)-N(1A)	110.7 (3)
O(21A)-P(2A)-N(3A)	107.4 (2)	O(22A)-P(2A)-N(1A)	109.6 (3)
O(22A)-P(2A)-N(3A)	107.8 (2)	O(22A)-P(2A)-O(21A)	103.4 (2)
P(2A)-N(1A)-P(6A)	122.0 (3)	P(2A)-N(3A)-P(4A)	121.3 (3)
P(4A)-N(5A)-P(6A)	118.8 (3)	C(41A)-N(41A)-P(4A)	119.8 (4)
C(47A)-N(41A)-P(4A)	120.3 (4)	C(47A)-N(41A)-C(41A)	110.5 (5)
C(61A)-N(61A)-P(6A)	120.7 (5)	C(67A)-N(61A)-P(6A)	121.0 (5)
C(67A)-N(61A)-C(61A)	111.2 (6)	C(22A)-O(22A)-P(2A)	116.6 (3)
C(21A)-O(21A)-P(2A)	117.7 (3)	C(23A)-C(22A)-O(22A)	108.9 (5)
C(23A)-C(21A)-O(21A)	110.3 (5)	C(22A)-C(23A)-O(21A)	112.2 (5)
C(22A)-C(23A)-C(21A)	112.2 (5)	C(67A)-C(65A)-C(63A)	110.6 (9)
C(65A)-C(63A)-C(61A)	109.1 (7)	C(43A)-C(41A)-N(41A)	103.9 (5)
C(65A)-C(67A)-N(61A)	104.4 (8)	C(47A)-C(45A)-C(43A)	106.4 (6)
C(45A)-C(43A)-C(41A)	107.6 (6)	C(21B)-O(21B)-P(2B)	116.7 (4)
C(45A)-C(47A)-N(41A)	104.4 (5)	C(23B)-C(22B)-O(22B)	111.4 (6)
N(5B)-P(6B)-Cl(6B)	105.3 (3)	C(23B)-C(21B)-O(21B)	110.9 (7)
N(1B)-P(6B)-N(5B)	119.7 (3)	C(65B)-C(63B)-C(61B)	108.2 (8)
N(61B)-P(6B)-N(5B)	110.5 (3)	C(65B)-C(67B)-N(61B)	102.6 (6)
N(5B)-P(4B)-Cl(4B)	105.2 (3)	C(45B)-C(43B)-C(41B)	107.0 (8)
N(3B)-P(4B)-N(5B)	119.2 (3)	C(45B)-C(47B)-N(41B)	104.0 (6)
N(41B)-P(4B)-N(5B)	110.4 (3)	C(21B)-O(21B)-P(2B)	116.7 (4)
N(1B)-P(2B)-N(3B)	117.2 (2)	C(21B)-C(23B)-C(22B)	110.0 (6)
O(22B)-P(2B)-N(1B)	108.2 (3)	C(63B)-C(61B)-N(61B)	103.6 (6)
O(21B)-P(2B)-N(1B)	107.3 (3)	C(67B)-C(65B)-C(63B)	111.0 (0)
P(2B)-N(5B)-P(6B)	119.1 (3)	C(43B)-C(41B)-N(41B)	103.8 (6)
P(2B)-N(1B)-P(6B)	121.8 (3)	C(45B)-C(43B)-C(41B)	109.9 (8)
C(67B)-N(61B)-P(6B)	122.7 (5)		
C(41B)-N(41B)-P(4B)	123.2 (4)		
C(47B)-N(41B)-C(41B)	109.6 (5)		
C(22B)-O(22B)-P(2B)	118.4 (4)		

34 H atoms out of 56 were located at this stage from a difference map, all the H atoms were restricted to idealized positions (C-H = 1.08 Å) and refinement converged to a final R value of 4.4% and wR = 4.9% (H atoms isotropic, others anisotropic). The positional and equivalent thermal parameters and bond lengths and angles are listed in Tables 2 and 3. Fig. 1 shows the averaged molecular dimensions.

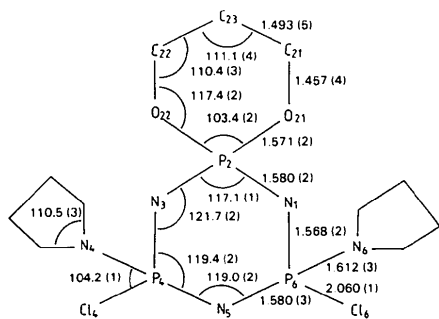


Fig. 1. Averaged molecular dimensions (\AA , $^\circ$) of (4).

(5) Six phosphorus atoms out of 62 non-H atoms of the asymmetric unit (two independent molecules) were located from the best E map. Several cycles of refinement, followed by a difference synthesis revealed

Table 4. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for compound (5)

U_{eq} according to Hamilton (1959).			
	<i>x</i>	<i>y</i>	<i>z</i>
P(6A)	1123 (1)	1932 (1)	9248 (1)
P(4A)	-1034 (1)	2690 (1)	9111 (1)
P(2A)	-131 (1)	1061 (1)	7804 (1)
N(1A)	842 (3)	1042 (2)	8391 (2)
N(3A)	-1066 (3)	1862 (2)	8168 (2)
N(5A)	125 (3)	2719 (2)	9600 (2)
N(61A)	1147 (3)	1641 (3)	10049 (2)
N(62A)	2654 (3)	2339 (3)	9069 (2)
N(41A)	-2504 (3)	2594 (2)	9623 (2)
N(42A)	-945 (3)	3744 (2)	9112 (2)
O(22A)	641 (3)	1076 (2)	6925 (2)
O(21A)	-1007 (3)	91 (2)	7497 (2)
C(21A)	-400 (5)	-743 (3)	6869 (3)
C(23A)	244 (5)	-586 (3)	6097 (3)
C(22A)	1249 (5)	230 (3)	6325 (3)
C(61A)	169 (6)	1813 (5)	10773 (4)
C(63A)	663 (10)	1456 (7)	11331 (5)
C(65A)	1722 (9)	940 (8)	10862 (5)
C(67A)	2042 (5)	992 (4)	10013 (4)
C(62A)	3270 (5)	2263 (4)	8216 (3)
C(64A)	4484 (7)	2886 (6)	8359 (5)
C(66A)	4186 (6)	3662 (5)	9228 (6)
C(68A)	3200 (5)	3213 (4)	9732 (4)
C(41A)	-3233 (5)	1670 (4)	9459 (4)
C(43A)	-3952 (9)	1666 (7)	10249 (6)
C(45A)	-3760 (8)	2583 (7)	10888 (5)
C(47A)	-2804 (5)	3215 (5)	10550 (3)
C(42A)	350 (4)	4163 (3)	8847 (3)
C(44A)	-8 (6)	4900 (4)	8587 (4)
C(46A)	-1271 (6)	4510 (4)	8257 (4)
C(48A)	-1974 (5)	4014 (3)	8802 (3)
P(2B)	6573 (1)	1889 (1)	5323 (1)
P(4B)	6571 (1)	2436 (1)	3997 (1)
P(6B)	5104 (1)	3332 (1)	5598 (1)
N(1B)	5656 (3)	2677 (2)	5928 (2)
N(3B)	7004 (3)	1769 (2)	4372 (2)
N(5B)	5573 (3)	3177 (2)	4628 (2)
N(41B)	7956 (3)	2900 (2)	3664 (2)
N(42B)	5912 (3)	1838 (2)	3109 (2)
N(61B)	5436 (4)	4441 (3)	6208 (3)
N(62B)	3509 (4)	3196 (3)	5804 (3)
O(21B)	5927 (3)	901 (2)	5307 (2)
O(22B)	7866 (2)	2029 (2)	5742 (2)
C(21B)	7706 (4)	1891 (3)	6532 (3)
C(22B)	5745 (5)	778 (3)	6101 (3)
C(23B)	7051 (5)	941 (3)	6417 (3)
C(41B)	9024 (4)	3265 (4)	4155 (3)
C(43B)	9770 (10)	3942 (8)	3855 (7)
C(45B)	9238 (6)	4027 (5)	3205 (5)
C(47B)	7939 (5)	3486 (4)	3161 (4)
C(42B)	4494 (4)	1551 (3)	3146 (3)
C(44B)	4339 (5)	856 (5)	2258 (4)
C(46B)	5545 (6)	387 (4)	1968 (4)
C(48B)	6597 (5)	1070 (4)	2397 (3)
C(61B)	6187 (10)	5129 (5)	5967 (5)
C(63B)	6272 (9)	6030 (5)	6767 (6)
C(65B)	6368 (12)	5673 (5)	7371 (6)
C(67B)	5140 (14)	4845 (6)	7202 (6)
C(64B)	1412 (7)	2421 (8)	5885 (8)
C(66B)	1323 (6)	3121 (6)	5643 (7)
C(68B)	2642 (6)	3629 (7)	5616 (8)

the remaining non-H atoms. All the H atoms were restricted to idealized positions (C-H = 0.96 Å) and refinement converged to a final *R* value of 5.9% and *wR* = 6.5% (H atoms isotropic, others anisotropic). The positional and equivalent thermal parameters and bond lengths and angles are listed in Tables 4 and 5 and Fig. 2 shows the averaged molecular dimensions.

The calculations were performed on a DEC VAX11/750 computer using the *SHELX76* (Sheldrick, 1976) and *SHELX80* (Sheldrick, 1980) program systems. Neutral-atom scattering factors were taken from

Table 5. Bond lengths (Å) and bond angles (°) for compound (5)

N(1A)-P(6A)	1.592 (3)	N(5A)-P(6A)	1.592 (3)
N(61A)-P(6A)	1.639 (4)	N(62A)-P(6A)	1.646 (3)
N(3A)-P(4A)	1.610 (3)	N(5A)-P(4A)	1.586 (4)
N(41A)-P(4A)	1.641 (3)	N(42A)-P(4A)	1.643 (4)
N(1A)-P(2A)	1.578 (4)	N(3A)-P(2A)	1.561 (3)
O(22A)-P(2A)	1.591 (3)	O(21A)-P(2A)	1.579 (2)
C(61A)-N(61A)	1.419 (7)	C(67A)-N(61A)	1.466 (8)
C(62A)-N(62A)	1.460 (7)	C(68A)-N(62A)	1.485 (6)
C(41A)-N(41A)	1.465 (6)	C(47A)-N(41A)	1.492 (6)
C(42A)-N(42A)	1.485 (5)	C(48A)-N(42A)	1.476 (7)
C(22A)-O(22A)	1.456 (5)	C(21A)-O(21A)	1.455 (5)
C(23A)-C(21A)	1.479 (7)	C(22A)-C(23A)	1.483 (6)
C(63A)-C(61A)	1.499 (15)	C(65A)-C(63A)	1.394 (14)
C(67A)-C(65A)	1.479 (12)	C(64A)-C(62A)	1.462 (9)
C(66A)-C(64A)	1.503 (10)	C(68A)-C(66A)	1.505 (10)
C(43A)-C(41A)	1.434 (12)	C(45A)-C(43A)	1.413 (12)
C(47A)-C(45A)	1.508 (12)	C(44A)-C(42A)	1.524 (10)
C(46A)-C(44A)	1.472 (9)	C(48A)-C(46A)	1.485 (9)
N(1B)-P(2B)	1.571 (3)	N(3B)-P(2B)	1.564 (3)
O(21B)-P(2B)	1.580 (3)	O(22B)-P(2B)	1.592 (3)
N(3B)-P(4B)	1.600 (4)	N(5B)-P(4B)	1.593 (3)
N(41B)-P(4B)	1.650 (3)	N(42B)-P(4B)	1.643 (3)
N(1B)-P(6B)	1.589 (5)	N(5B)-P(6B)	1.586 (4)
N(61B)-P(6B)	1.635 (3)	N(62B)-P(6B)	1.634 (4)
C(41B)-N(41B)	1.457 (6)	C(47B)-N(41B)	1.469 (9)
C(42B)-N(42B)	1.473 (5)	C(48B)-N(42B)	1.481 (5)
C(61B)-N(61B)	1.392 (9)	C(67B)-N(61B)	1.553 (10)
C(62B)-N(62B)	1.545 (9)	C(68B)-N(62B)	1.373 (13)
C(22B)-O(21B)	1.443 (6)	C(21B)-O(22B)	1.449 (6)
C(23B)-C(21B)	1.485 (7)	C(23B)-C(22B)	1.508 (7)
C(43B)-C(41B)	1.433 (14)	C(45B)-C(43B)	1.406 (17)
C(47B)-C(45B)	1.476 (8)	C(44B)-C(42B)	1.489 (7)
C(46B)-C(44B)	1.461 (9)	C(48B)-C(46B)	1.472 (7)
C(63B)-C(61B)	1.516 (9)	C(65B)-C(63B)	1.403 (17)
C(67B)-C(65B)	1.643 (15)	C(64B)-C(62B)	1.543 (11)
C(66B)-C(64B)	1.352 (19)	C(68B)-C(66B)	1.479 (10)
N(5A)-P(6A)-N(1A)	116.3 (2)	N(61A)-P(6A)-N(1A)	112.6 (2)
N(62A)-P(6A)-N(5A)	105.5 (2)	N(62A)-P(6A)-N(1A)	106.0 (2)
N(61A)-P(6A)-N(5A)	113.3 (2)	N(62A)-P(6A)-N(61A)	102.5 (2)
N(5A)-P(4A)-N(3A)	115.9 (2)	N(41A)-P(4A)-N(3A)	105.0 (2)
N(41A)-P(4A)-N(5A)	114.4 (2)	N(42A)-P(4A)-N(3A)	112.8 (2)
N(42A)-P(4A)-N(5A)	105.7 (2)	N(42A)-P(4A)-N(41A)	102.3 (2)
N(3A)-P(2A)-N(1A)	118.9 (2)	O(22A)-P(2A)-N(1A)	110.9 (2)
O(22A)-P(2A)-N(3A)	106.6 (2)	O(21A)-P(2A)-N(1A)	109.0 (2)
O(21A)-P(2A)-N(3A)	107.6 (2)	O(21A)-P(2A)-O(22A)	102.5 (1)
P(2A)-N(1A)-P(6A)	121.2 (2)	P(2A)-N(3A)-P(4A)	122.1 (2)
P(4A)-N(5A)-P(6A)	123.6 (2)	C(61A)-N(61A)-P(6A)	125.1 (4)
C(67A)-N(61A)-P(6A)	122.7 (3)	C(67A)-N(61A)-C(61A)	111.0 (5)
C(62A)-N(62A)-P(6A)	122.0 (3)	C(68A)-N(62A)-P(6A)	119.4 (3)
C(68A)-N(62A)-C(62A)	110.0 (4)	C(41A)-N(41A)-P(4A)	120.8 (3)
C(47A)-N(41A)-P(4A)	119.8 (3)	C(47A)-N(41A)-C(41A)	108.9 (4)
C(42A)-N(42A)-P(4A)	118.2 (3)	C(48A)-N(42A)-P(4A)	120.9 (3)
C(48A)-N(42A)-C(42A)	109.2 (4)	C(22A)-O(22A)-P(2A)	117.3 (3)
C(21A)-O(21A)-P(2A)	118.5 (2)	C(23A)-C(21A)-O(21A)	110.6 (4)
C(22A)-C(23A)-C(21A)	110.7 (4)	C(23A)-C(22A)-O(22A)	109.9 (4)
C(63A)-C(61A)-N(61A)	104.7 (6)	C(65A)-C(63A)-C(61A)	108.6 (8)
C(67A)-C(65A)-C(63A)	109.9 (10)	C(65A)-C(67A)-N(61A)	103.9 (5)
C(64A)-C(62A)-N(62A)	105.0 (5)	C(66A)-C(64A)-C(62A)	105.1 (5)
C(68A)-C(66A)-C(64A)	105.4 (6)	C(66A)-C(68A)-N(62A)	104.2 (5)
C(43A)-C(41A)-N(41A)	109.2 (5)	C(45A)-C(43A)-C(41A)	107.4 (8)
C(47A)-C(45A)-C(43A)	111.9 (7)	C(45A)-C(47A)-N(41A)	102.5 (5)
C(44A)-C(42A)-N(42A)	103.1 (4)	C(46A)-C(44A)-C(42A)	104.6 (6)
C(48A)-C(46A)-C(44A)	105.1 (6)	C(46A)-C(48A)-N(42A)	105.7 (4)
N(3B)-P(2B)-N(1B)	119.0 (2)	O(21B)-P(2B)-N(1B)	109.9 (2)
O(22B)-P(2B)-N(1B)	107.4 (2)	O(22B)-P(2B)-N(1B)	109.5 (2)
O(22B)-P(2B)-N(3B)	107.6 (2)	N(41B)-P(4B)-N(3B)	104.9 (2)
N(5B)-P(4B)-N(3B)	115.9 (2)	N(41B)-P(4B)-N(5B)	112.6 (2)
N(41B)-P(4B)-N(5B)	114.8 (2)	N(42B)-P(4B)-N(3B)	101.1 (2)
N(42B)-P(4B)-N(5B)	106.7 (2)	N(42B)-P(4B)-N(41B)	101.1 (2)
N(5B)-P(6B)-N(1B)	116.4 (2)	N(61B)-P(6B)-N(1B)	110.4 (2)
N(61B)-P(6B)-N(5B)	108.7 (2)	N(62B)-P(6B)-N(1B)	106.3 (2)
N(62B)-P(6B)-N(5B)	111.9 (2)	N(62B)-P(6B)-N(61B)	102.2 (2)
P(6B)-N(1B)-P(2B)	122.4 (2)	P(2B)-N(3B)-P(2B)	122.3 (2)
P(6B)-N(5B)-P(4B)	123.8 (3)	C(41B)-N(41B)-P(4B)	119.5 (3)
C(47B)-N(41B)-P(4B)	120.2 (3)	C(47B)-N(41B)-C(41B)	109.7 (4)
C(48B)-N(42B)-P(4B)	120.3 (3)	C(48B)-N(42B)-P(4B)	119.7 (3)
C(48B)-N(42B)-C(42B)	108.2 (3)	C(61B)-N(61B)-P(6B)	127.5 (4)
C(67B)-N(61B)-P(6B)	123.0 (5)	C(67B)-N(61B)-C(61B)	108.7 (5)
C(62B)-N(62B)-P(6B)	118.7 (4)	C(68B)-N(62B)-P(6B)	125.7 (6)
C(68B)-N(62B)-C(62B)	109.4 (5)	C(22B)-O(21B)-P(2B)	117.1 (2)
C(21B)-O(22B)-P(2B)	116.7 (2)	C(23B)-C(21B)-O(22B)	111.0 (3)
C(23B)-C(22B)-O(21B)	109.5 (4)	C(22B)-C(23B)-C(21B)	111.5 (5)

Table 5 (cont.)

C(43B)-C(41B)-N(41B) 103.5 (7)	C(45B)-C(43B)-C(41B) 113.2 (8)
C(47B)-C(45B)-C(43B) 106.1 (8)	C(45B)-C(47B)-N(41B) 104.7 (6)
C(44B)-C(42B)-N(42B) 103.8 (3)	C(46B)-C(44B)-C(42B) 103.9 (5)
C(48B)-C(46B)-C(44B) 107.8 (5)	C(46B)-C(48B)-N(42B) 104.9 (4)
C(63B)-C(61B)-N(61B) 107.7 (6)	C(65B)-C(63B)-C(61B) 100.9 (7)
C(67B)-C(65B)-C(63B) 101.0 (9)	C(65B)-C(67B)-N(61B) 95.6 (7)
C(64B)-C(62B)-N(62B) 98.3 (7)	C(66B)-C(64B)-C(62B) 111.3 (8)
C(68B)-C(66B)-C(64B) 107.2 (9)	C(66B)-C(68B)-N(62B) 109.4 (10)

Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) for the non-H and H atoms respectively.* Figures were drawn using *CHEMGRAPH* (Davies, 1983) program suite.

Discussion of structures

A priori, one would have expected that replacement of the electron-withdrawing chlorine atoms by the strongly electron-releasing pyrrolidino groups would displace electron density towards, and within, the six-membered phosphate ring. We indeed note that in the asymmetric segments $(\text{CH}_2)_3\text{O}_2\text{P}-\text{N}-\text{PXY}$ [$X = Y = \text{Cl}$, (2); $X = \text{Cl}$, $Y = \text{pyr}$, (4); $X = Y = \text{pyr}$ (5)], the $(\text{CH}_2)_3\text{O}_2\text{P}-\text{N}$ bond is the longer one in compound (2), whilst progressive substitution of Cl atoms by pyrrolidino groups diminishes the difference in the three-atom segments in compound (4), and finally reverses the bond-length pattern in compound (5).

We have called this difference $\Delta(\text{P}-\text{N})$ [for definitions see Contractor, Hursthouse, Shaw, Shaw & Yilmaz (1985) and Fincham, Hursthouse, Parkes, Shaw & Shaw (1986)]. $\Delta(\text{P}-\text{N})$ for compounds (2), (4) and (5) is 0.021 (4), 0.012 (3) and -0.029 (3) Å, respectively (Table 6). Concomitant with increasing electron-density at the spiro P atom, the back-donations of the lone pairs of electrons on the O atoms

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data, dihedral angles, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44421 (88 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

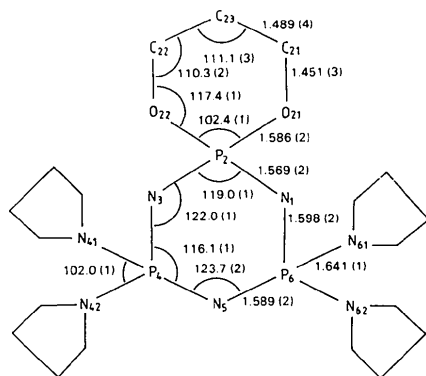


Fig. 2. Averaged molecular dimensions (Å, °) of (5).

Table 6. Comparisons of selected bond lengths (Å) and angles (°)

	$(\text{CH}_2)_3\text{O}_2\text{P}-\text{N}$	$\text{N}-\text{PXY}$	$\Delta(\text{P}-\text{N})$	$\text{P}-\text{O}$	$\text{N}(1)-\text{P}(2)-\text{N}(3)$	OPO
(2)	1.582 (4)	1.561 (4)	0.021 (4)	1.551 (3)	116.6 (3)	105.4 (3)
(4)	1.580 (2)	1.568 (2)	0.012 (3)	1.571 (2)	117.1 (1)	103.4 (2)
(5)	1.569 (2)	1.598 (2)	-0.029 (3)	1.586 (2)	119.0 (1)	102.4 (1)

towards the P atom is decreased, and we observe an increase in $\text{P}-\text{O}$ bond length on passing from compound (2) to (4) and then to (5) (Table 6).

This increase in electron density in the $\text{P}-\text{N}$ bonds at the spiro atom (2→4→5) widens the *endo* NPN angle (Table 6). The corresponding decrease of electron density in the $\text{P}-\text{O}$ bonds is accompanied by a decrease in the OPO bond angle in the same series of compounds (Table 6). At the opposite N atom [N(5)] in the cyclotriphosphazatriene ring the *endo* angle $\text{P}(4)-\text{N}(5)-\text{P}(6)$ increases considerably to 123.7 (2)° in compound (5). This is accompanied by a decrease [in compound (5)] of the *endo* angle $\text{N}(3)-\text{P}(4)-\text{N}(5)$ to 116.1 (1)°, whilst in the other two structures, (2) and (4), this angle is larger at 119.2 (2) and 119.4 (2)°, respectively.

The $\text{P}-\text{Cl}$ bonds behave in a, by now, expected manner. They are relatively short in the PCl_2 group [1.986 (2) Å], and considerably lengthened in the PClpyr moiety [2.060 (1) Å]. We have learned to associate this with different ^{35}Cl NQR frequency ranges [PCl_2 26–30, $\text{PCl}(\text{NR}_2)$ 23–24 MHz] and hence with a greater degree of ionic character in the $\text{P}-\text{Cl}$ bond (Keat, Porte, Tong & Shaw, 1972). Because of the electron-withdrawing power of the Cl atoms the exocyclic $\text{P}-\text{N}$ bond in compound (4) is shorter [1.612 (3) Å] than the corresponding bonds in compound (5) [1.641 (1) Å].

The exocyclic bond angle NPN [102.0 (1)°] in (5) is larger than the exocyclic bond angle CIPC1 [100.2 (1)°] in (2), in keeping with the greater back-donation of lone-pair electrons from the N atoms. This is also reflected in the internal NPN and PNP bond angles of these two compounds (see above). In compound (4) the exocyclic bond angle NPC1 [104.2 (1)°] is considerably larger than the corresponding angles in compounds (2) and (5). This, together with the relatively small changes in the endocyclic NPN and PNP bond angles, suggests that the electron donation from the pyrrolidino group in compound (4) is largely transferred to the adjacent $\text{P}-\text{Cl}$ bond and only to a lesser extent to the N_3P_3 ring.

Conformation

The 1,3-propanedioxy ring remains in the chair conformation and the N_3P_3 ring is planar in all three compounds [(2), (4) and (5)]. The molecular diagrams for (4) and (5) are in Figs. 3 and 4. The OPO plane is perpendicular to the adjacent NPN plane in compounds

(2), (4) and (5), and the dihedral angles, POCC, are given in Table 7.

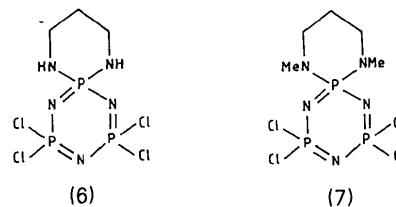
The relationship of P–O bond lengths and $^3J(\text{POCC})$ spin–spin coupling constants in solution

We have shown elsewhere (Deutsch, Hursthouse, Kılıç, Parkes, Shaw & Shaw, 1987) that the three-bond spin–spin coupling constant, $^3J(\text{PNCC})$, is not only a function of the dihedral angle, PNCC [the Karplus relationship (Karplus, 1959, 1960, 1963; Davies & Sadikot, 1982; Lankhorst, Haasnoot, Erkelens & Altona, 1984)], but is also dependent on the stereochemistry of the N atom and the P–N bond length. Thus in the spiro derivatives $\text{N}_3\text{P}_3[\text{NH}(\text{CH}_2)_3\text{NH}]\text{Cl}_4$ (6) and $\text{N}_3\text{P}_3[\text{NMe}(\text{CH}_2)_3\text{NMe}]\text{Cl}_4$ (7) the spin–spin coupling constants, $^3J(\text{PNCC})$, are 6.5 and 2.3 Hz, respectively. The dihedral angles PNCC are 62 (6) and 49 (7)°. One would thus have expected a slightly larger $^3J(\text{PNCC})$ value for (7) than for (6); instead a drastic decrease was observed. We related this to the increase in the P–N bond length [(6), 1.618 (6); (7) 1.637 (3) Å] and the change of stereochemistry of the N atom [the sums of the bond angles around the N atoms are (6), 359.9 (1.2); (7) 351.0 (2.3)°]. The N

Table 7. POCC dihedral angles (°) for compounds (2), (4) and (5) (e.s.d.'s ~2°)

Compound (2)	Compound (4)	Compound (5)
P(2)O(2)C(21)C(22)	54	55
P(2A)O(21A)C(21A)C(23A)	55	55
P(2A)O(22A)C(22A)C(23A)	58	58
P(2B)O(21B)C(21B)C(23B)	59	59
P(2B)O(22B)C(22B)C(23B)	53	56

atoms of (7) lie 0.260 (3) Å out of the planes of their three bonding partners.



In the bicyclic structures $\text{N}_4\text{P}_4(\text{NMe}_2)_5(\text{NHet})(\text{NEt})$ (8) and $\text{N}_4\text{P}_4(\text{NHet})_6(\text{NEt})$ (9) (Deutsch, Hursthouse, Kılıç, Parkes, Shaw & Shaw, 1987) the P–N bonds to the N–Et groups (assumed to rotate freely) are in the range 1.699–1.724 Å (bridging N atoms) and 1.624–1.636 Å (bridgehead substituents), the sums of the bond angles around the respective N atoms are 339.5–340.5 (3–5)° (bridging) and 359.8 (2.8)° (bridgehead). The relevant spin–spin coupling constants $^3J(\text{PNCC})$ are 2.4–2.6 and 7.3–9.0 Hz.

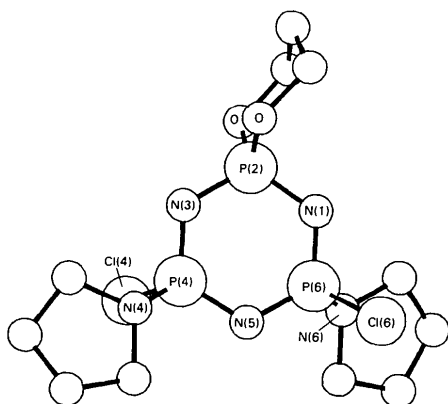
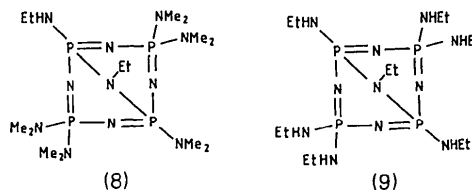


Fig. 3. Molecular diagram of (4).

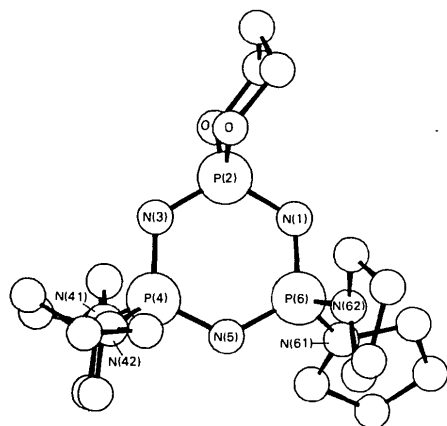


Fig. 4. Molecular diagram of (5).

Clearly, apart from dihedral-angle changes, lengthening of the P–N bond and/or changing the stereochemistry of the N atom from trigonal planar towards pyramidal, decreases the three-bond spin–spin coupling constants, $^3J(\text{PNCC})$. Karplus himself (1959, 1960, 1963) has drawn attention to the fact that dihedral angles are not the only parameter determining vicinal coupling constants, and *inter alia* referred to hybridization and bond length. These effects were, however, subsequently largely ignored, though empirical factors were introduced to obtain better fits for some systems [for a discussion of these and electronegativity corrections see Davies & Sadikot (1982)].

It is well known that lone pairs of electrons on N atoms can back-donate much more effectively than can lone pairs of O atoms. One would therefore, *a priori*, expect to see smaller changes in the POCC system and this is what is observed.

We cannot comment on the stereochemistry of the O atoms. The POC bond angles are virtually constant: (2)

117.6 (4), (4) 117.4 (2), (5) 117.4 (1)°. The P—O bond lengths increase from (2) 1.551 (3) Å to (5) 1.586 (2) Å (Table 6) in line with increasing electron supply. This is reflected in a decrease in the three-bond spin-spin coupling constant, $^3J(\text{POCC})$, which varies from (2) 7.35 Hz to (4) 6.45 Hz and to (5) 5.9 Hz. The average POCC dihedral angles change from (2) 54.4° to (4) 56.3° and (5) 57.2°. If no factors other than dihedral angles affected the vicinal coupling constants, a marginal overall decrease of 0.3–0.4 Hz would have been expected. The considerably larger changes observed must be attributed to the P—O bond lengthening with increasing electron supply to the P atom.

The decrease in $^3J(\text{POCC})$ and $^3J(\text{PNCC})$ spin-spin coupling constants with increased P—O and P—N bond lengths, respectively, indicates the importance of Fermi contact. The large Fermi contact contributions to coupling constants in cyclophosphazenes have been established experimentally and theoretically by Thomas, Grossmann & Meyer (1981).

$^3J(\text{POCC})$ spin-spin coupling constants are widely used to obtain information about conformation; this includes molecules of biological importance. Our results show that factors other than dihedral angles affect vicinal coupling constants, and these must be taken into consideration. However, in most other phosphorus systems, changes in electron supply towards the P—O bond will be much less than in phosphazene derivatives, hence changes in P—O bond lengths would be smaller and therefore more difficult to observe.

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Cryocrystallography of Biological Macromolecules: a Generally Applicable Method

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Abstract

Methods have been developed that allow facile X-ray data collection for biological macromolecules at

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