617. The Crystal and Molecular Structure of Tetrameric Phosphonitrilic Dimethylamide (Octakisdimethylaminocyclotetraphosphazatetraene).

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Crystals of tetrameric phosphonitrilic dimethylamide, $P_4N_4(NMe_2)_8$, are tetragonal, $a = 13{\cdot}00$, $c = 8{\cdot}59$ Å, space group $I\bar{4}$ with two molecules in the unit cell, molecular symmetry $\bar{4}$ (S_4). The atomic positions have been determined by Fourier and least-squares refinement of *X*-ray diffraction data. The molecule has a puckered eight-membered ring of alternate phosphorus and nitrogen atoms, P–N bond length 1·58 Å. The exocyclic P–N bonds are 1·67 and 1·69 Å long, considerably shorter than the accepted P–N single-bond length (1·77 Å). It is suggested that this shortening is due to (i) the phosphorus atom's being in the sp^3-hybrid state and forming $p\pi$-$d\pi$-bonds with the cyclic nitrogen, and (ii) a tendency of the exocyclic P–N bond to double-bond character as a result of donation of electrons from the lone pair of the exocyclic nitrogen. The more important valency angles are: N–P–N (cyclic) 120°, P–N–P (cyclic) 133°, N–P–N (exocyclic) 104°.

ALTHOUGH the phosphonitrilic halides have been known for many years there has until recently been comparatively little interest in them and their derivatives, and very few of their crystal structures have been examined. Craig's proposal [1] that these compounds are aromatic in character and that aromaticity is not, as with carbon systems, confined to six-membered rings, has created a need for knowledge of their precise stereochemistry. Until two years ago the only detailed crystal structure determination of a phosphonitrilic compound was that of $(PNCl_2)_4$ by Ketelaar and de Vries.[2] This has recently been refined by Hazekamp *et al.*[3] and in addition there are *X*-ray diffraction studies of $(PNCl_2)_3$ (Wilson

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[1] Craig, *J.*, 1959, 997.

[2] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

[3] Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539.

and Carroll[4]), $(PNF_2)_4$ (McGeachin and Tromans[5]), $P_4N_4Me_8$ (Dougill[6]), and the present work on $P_4N_4(NMe_2)_8$ (the preliminary results of which have already been published[7]). Of the four tetrameric derivatives examined, $(PNF_2)_4$ has a planar ring, while the other three have puckered rings with very similar bond lengths and angles.

EXPERIMENTAL

The preparation of the amide $P_4N_4(NMe_2)_8$ has been described by Ray and Shaw.[8] Crystals suitable for *X*-ray examination were grown from a solution in toluene. They are colourless tetragonal needles, the forms developed being the tetragonal prism {110} and tetragonal bisphenoid {101}. Two crystals were used to provide equi-inclination Weissenberg photographs (Cu-*K* radiation, multiple-film technique, room temperature) for measurement of unit-cell dimensions and intensities: (i) a needle which had been reduced to a cylinder (axis parallel to *c*) of diameter 0·1 mm. by rotating it against a strip of filter paper wetted with toluene, for (*hk*0), (*hk*2), and (*hk*3) layers, and (ii) a roughly equidimensional prism cut from a needle of diameter 0·1 mm., for (0*kl*), (1*kl*), and (2*kl*) layers. It was considered that, with these crystals, absorption errors would be inappreciable. Intensities were estimated visually and corrected for variation in reflexion spot-shape on upper layer lines as proposed by Phillips.[9] From a total of 754 independent reflexions with the limiting sphere, the intensities of 556 were measured, and of these only 21 were too weak to be observed.

The three-dimensional refinement was carried out on the University of London Mercury computer by the method of least squares. The atomic scattering factors used were: phosphorus from tables,[10] nitrogen that of Freeman,[11] and carbon and hydrogen those of McWeeny.[12] Details of the computer programmes used for the refinement and for calculation of Fourier synthesis, molecular dimensions, and analysis of thermal motion have been given by Mills and Rollet.[13]

The diamagnetic anisotropy was measured by the critical torsion method.[14] A crystal large enough for this purpose was grown by stirring 1—2 c.c. of a saturated solution in toluene in which had been placed a number of small crystal fragments and one larger well-shaped crystal. The large crystal grew, at the expense of the fragments, to a length of 3 mm. Crystals grown in this agitated solution had a more perfect development of external faces than those grown in a stationary solution. The anisotropy was found to be $\chi_{\parallel} - \chi_{\perp} = -5 \times 10^{-6}$ c.g.s.e.m.u., so that the crystal is magnetically negative. With a crystal of the size used and this low anisotropy, the critical torsion angle is small so that the result is only approximate.

The melting point of $P_4N_4(NMe_2)_8$ has been given [8] as 237° but the melting is accompanied by decomposition from about 220° and takes place over a range of temperature. There is, however, a transition point, which has not hitherto been reported, at 112°. At this temperature the substance passes from the tetragonal phase described in this paper into an isotropic phase. This change, which can be observed under the microscope (from loss of polarization colours), occurs quite sharply without decomposition and is reversible; it is therefore a better criterion for identification than the melting point with decomposition.

Crystal Data.—$P_4N_4(NMe_2)_8$, $M = 532{\cdot}6$, tetragonal bisphenoidal, $a = b = 13{\cdot}00 \pm 0{\cdot}01$, $c = 8{\cdot}59 \pm 0{\cdot}01$ Å, $U = 1452$ Å^3, $D_m = 1{\cdot}219$ g. cm.$^{-3}$ (by flotation), $Z = 2$, $D_c = 1{\cdot}218$ g. cm.$^{-3}$, $F(000) = 576$, $\mu = 25{\cdot}5$ cm.$^{-1}$ for Cu radiation. Space group $I\bar{4}$ (S_4^2, No. 82), systematic absences of *X*-ray reflexions: (*hkl*) absent when $h + k + l$ is odd, Laue symmetry $4/m$,

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[4] Wilson and Carroll, *J.*, 1960, 2548.
[5] McGeachin and Tromans, *J.*, 1961, 4777.
[6] Dougill, *J.*, 1961, 5471.
[7] Bullen, *Proc. Chem. Soc.*, 1960, 425.
[8] Ray and Shaw, *Chem. and Ind.*, 1959, 53.
[9] Phillips, *Acta Cryst.*, 1954, **7**, 746; 1956, **9**, 819.
[10] " Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935, p. 571.
[11] Freeman, *Acta Cryst.*, 1959, **12**, 261.
[12] McWeeny, *Acta Cryst.*, 1951, **4**, 513.
[13] (*a*) Cruickshank, Pilling, Bujosa, Lovell, and Truter, in " Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, London, 1961, p. 47; (*b*) Mills and Rollett, *ibid.*, pp. 122, 123.
[14] Krishnan and Banerjee, *Phil. Trans.*, 1934, **234***A*, 265.

molecular symmetry $\bar{4}$, optically uniaxial negative, refractive indices for sodium light $\varepsilon = 1{\cdot}550$, $\omega = 1{\cdot}570$.

STRUCTURE DETERMINATION

Since there are only two molecules in the body-centred unit cell, the molecules must occupy special positions on four-fold axes at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The projection of the structure on (001) was examined first because its symmetry is independent of whether the space group is $I4$, $I\bar{4}$, or $I4/m$, all of which are consistent with the systematic absences and Laue symmetry. The x- and y-co-ordinates of the phosphorus atoms were found from the (001) Patterson projection (Fig. 1), peak A being assigned to the vector between an atom at (x,y) and the related atom at $(\bar{y},x)$ and peak B to the vector between those at (x,y) and $(\bar{x},\bar{y})$. It later became evident that one carbon atom overlaps with the phosphorus in this projection, so that the P–P vectors are enhanced and their identification facilitated. From the co-ordinates of the phosphorus atom structure factors were calculated and their signs used to give a Fourier projection on (001) from which it was possible to locate the nitrogen and the carbon atoms. The projection was partially refined by Fourier and difference Fourier syntheses; during refinement it became clear that C(3), which had been placed incorrectly, must have almost the same x- and y-co-ordinates as the phosphorus atom. All other atoms are resolved in this projection (Fig. 2).

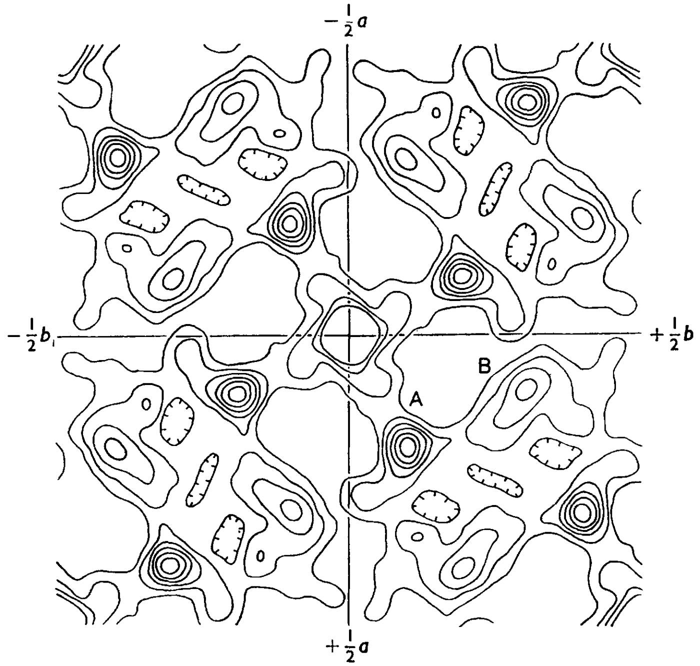

FIG. 1. Projection of the Patterson function on (001). Contour interval arbitrary; for clarity, the lower contours, and also those in the origin peak, are omitted.

From the appearance of the molecule in projection on (001) the following deductions were made regarding the molecular symmetry, leading to selection of $I\bar{4}$ as the correct space group, in agreement with the morphology. The eight P–N bonds in the ring are in two crystallographically non-equivalent sets of four with apparent lengths, in projection, of 1·6 and 1·35 Å. Space group $I4/m$ is rejected because it would require a planar P–N ring with these widely different lengths as the actual P–N bond lengths, and 1·35 Å is too short. Also, a planar P–N ring would result in a 002 reflexion much stronger than is observed. In $I4$ the four phosphorus atoms in the molecule would still be coplanar with their plane parallel to (001), but the four nitrogen atoms could lie in a different but parallel plane. The two P–N distances, however, would still be very different unless the two planes were very far apart, which is absurd; the length 1·35 Å could not be increased to a more reasonable value without making the other much greater than 1·6 Å. Hence $I4$ is rejected, leaving $I\bar{4}$ and molecular symmetry $\bar{4}$ as the only possibility. With this symmetry, by placing alternate phosphorus and nitrogen atoms of the ring above and below the (001) plane, one can have P–N bonds in the ring of more similar actual lengths but with the observed projected lengths.

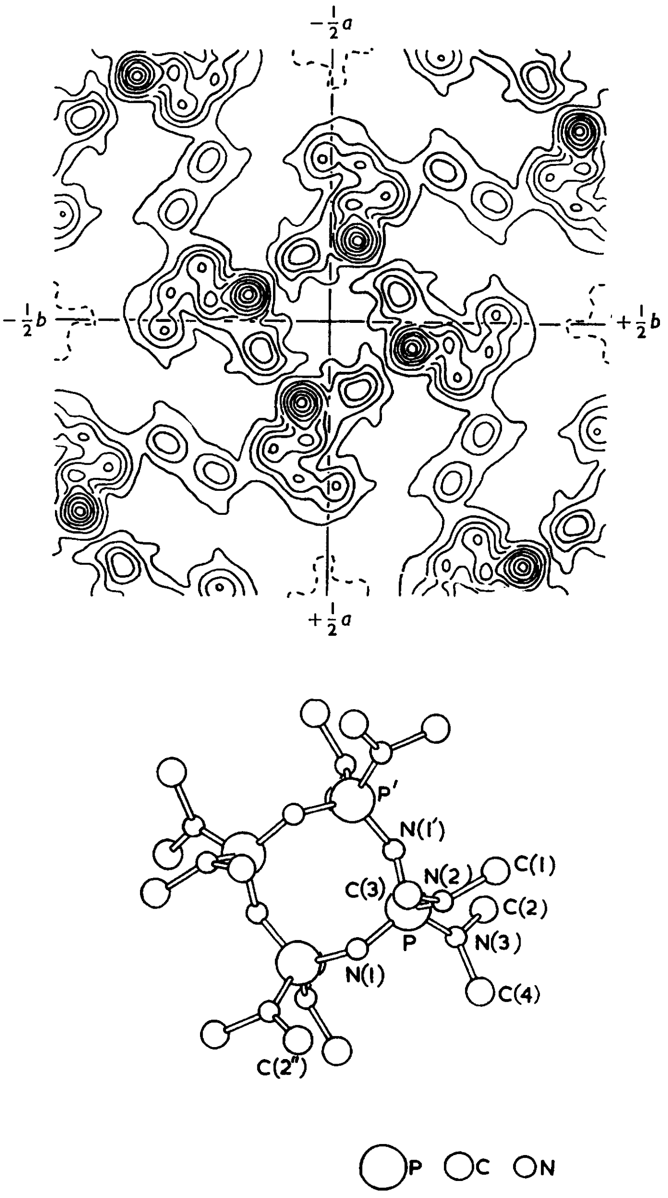

Fig. 2. Electron-density projection on (001). Contour interval 2eÅ^{-2} with the zero contour broken, except at phosphorus atoms where the contours are at 2, 5, 10, 15, 20, 25, 30eÅ^{-2}.

By using x- and y-co-ordinates derived from refinement of the (001) projection and assigning trial z co-ordinates to all atoms by taking likely values for bond lengths, $(0kl)$ structure factors were calculated. Good agreement with the observed values being obtained, the non-centrosymmetric $(0kl)$ projection (Fig. 3) was refined, partly by Fourier methods and partly by least squares.

When the R factor for the $(hk0)$ and $(0kl)$ intensities had fallen below 0·2, three-dimensional data were incorporated in the least-squares refinement. Using structure factors calculated with individual isotropic temperature factors for each atom and neglecting hydrogen atoms

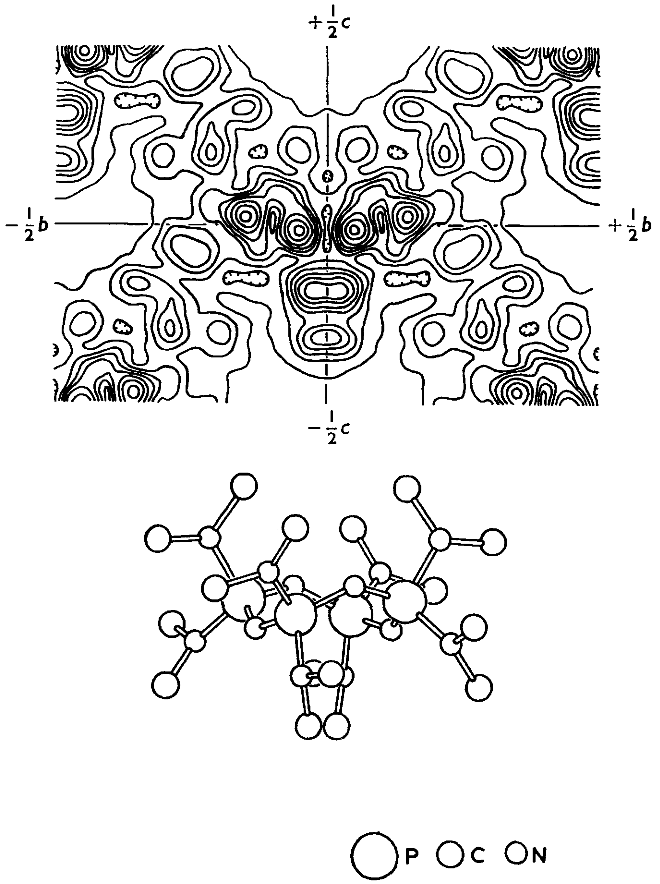

FIG. 3. Electron-density projection on (100). Contour interval 2eÅ^{-2} with the lowest contour at 2eÅ^{-2}. At the phosphorus atoms contours above 10eÅ^{-2} are at intervals of 5eÅ^{-2}.

enabled a three-dimensional difference Fourier synthesis to be performed. From it the positions of the hydrogen atoms in the methyl groups were found and suggestions for anisotropy of thermal motion were obtained. In assigning trial anisotropic temperature factors attempts were made to relate the anisotropy to the local molecular geometry, *e.g.*, for the exocyclic nitrogen atoms to place the maximum vibration direction as nearly as possible perpendicular to the three bonds formed by each such atom, provided this agreed with the difference Fourier. The introduction of hydrogen atoms and anisotropic temperature factors caused the R factors for the various layer lines (which were at this stage being refined separately) at first to rise slightly but in subsequent cycles R fell rapidly. For the final stages all the data were refined together.

Results.—The final atomic co-ordinates are given in Table 1. The co-ordinates adopted for hydrogen atoms (Table 2) are mostly those taken from the three-dimensional difference synthesis but some were adjusted slightly during refinement. They are not to be considered

TABLE 1.

Final atomic co-ordinates (expressed as fractions of unit-cell edges) and their standard deviations (in Å).

	x	*y*	*z*	σ(*x*) (Å)	σ(*y*) (Å)	σ(*z*) (Å)
P	+0·05005	+0·1480	+0·0208	0·0024	0·0024	0·0030
N(1)	+0·1254	+0·0567	+0·0603	0·009	0·009	0·010
N(2)	+0·0394	+0·2107	+0·1919	0·010	0·009	0·012
N(3)	+0·1047	+0·2343	−0·0972	0·009	0·009	0·010
C(1)	−0·0169	+0·3075	+0·1845	0·012	0·012	0·015
C(2)	+0·0543	+0·2865	−0·2203	0·012	0·013	0·016
C(3)	+0·0258	+0·1511	+0·3324	0·013	0·012	0·012
C(4)	+0·2051	+0·2774	−0·0496	0·012	0·013	0·015

TABLE 2.

Fractional co-ordinates of hydrogen atoms used for structure-factor calculations.

	x	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*
H(1) ...	+0·02	+0·33	+0·09	H(5) ...	+0·12	+0·31	−0·31	H(9) ...	+0·03	+0·20	+0·43
H(2) ...	−0·09	+0·29	+0·22	H(6) ...	+0·03	+0·37	−0·22	H(10) ...	+0·22	+0·36	−0·08
H(3) ...	+0·03	+0·36	+0·27	H(7) ...	−0·05	+0·13	+0·31	H(11) ...	+0·26	+0·22	−0·06
H(4) ...	−0·01	+0·26	−0·30	H(8) ...	+0·08	+0·08	+0·34	H(12) ...	+0·18	+0·30	+0·07

TABLE 3.

Components U_{ij} of thermal vibration tensors and their standard deviations (in 10^{-4} Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{23}	σ	U_{13}	σ	U_{12}	σ
P ...	306	7	277	7	438	8	−13	10	−3	10	−2	7
N(1) ...	458	35	512	36	575	44	0	41	7	36	−92	32
N(2) ...	573	38	482	32	588	45	−14	41	−74	45	21	31
N(3) ...	422	33	419	33	587	40	63	37	−84	37	−48	30
C(1) ...	491	45	530	43	751	57	−182	57	0	55	20	39
C(2) ...	606	50	629	52	777	73	235	60	−108	63	−202	44
C(3) ...	731	54	476	43	492	42	−44	49	14	58	−21	45
C(4) ...	508	44	569	48	738	68	−16	54	−5	54	−78	41

TABLE 4.

Amplitudes of thermal vibration (in Å) along the principal axes of the vibration ellipsoids. The direction of each principal axis is specified by the angles which it makes with the crystallographic axes.

	Å	*a*	*b*	*c*		Å	*a*	*b*	*c*
P	0·209	89°	86°	175°	C(1)	0·292	92°	119°	30°
	0·175	4	94	89		0·222	14	78	82
	0·166	86	6	85		0·206	104	32	62
N(1)	0·241	57	135	63	C(2)	0·324	64	126	133
	0·239	75	113	153		0·240	45	104	49
	0·197	37	53	92		0·197	56	40	108
N(2)	0·257	48	82	137	C(3)	0·271	7	95	86
	0·225	46	77	47		0·229	97	129	40
	0·218	105	15	93		0·210	91	140	130
N(3)	0·255	67	109	150	C(4)	0·272	91	85	174
	0·202	119	44	119		0·249	56	145	95
	0·193	39	52	83		0·213	35	56	87

as having been determined accurately; the C–H bond lengths calculated from them range from 1·0 to 1·2 Å. The anisotropic thermal parameters, together with standard deviations, are in Table 3. These U_{ij} values were used to calculate the orientation and magnitude of the principal axes of the vibration ellipsoid for each atom (Table 4). For hydrogen atoms an isotropic temperature factor $\exp(-5 \sin^2 \theta/\lambda^2)$ equivalent to $(\overline{u^2})^{\frac{1}{2}} = 0·25$ Å was used; it was not refined.

The observed and final calculated structure factors are in Table 5. The final *R* for all observed reflexions, except 110, 220, and 620, is 0·084. The 21 reflexions, which were too weak

TABLE 5.

Observed and calculated structure factors (× 5).

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
00*l*			
2	217	194	0°
4	242	242	0
6	150	131	0
8	50	47	180
10	32	25	0
01*l*			
1	671	680	354
3	309	303	9
5	150	151	20
7	66	67	268
9	40	37	348
11	9	9	295
02*l*			
0	<6	4	180
2	59	65	168
4	115	117	58
6	130	137	306
8	67	71	279
10	40	34	271
03*l*			
1	345	361	258
3	210	198	188
5	72	72	332
7	162	153	259
9	65	54	261
04*l*			
0	192	180	0
2	249	225	195
4	156	128	262
6	43	38	250
8	37	41	208
10	66	49	277
05*l*			
1	117	115	221
3	37	48	220
5	85	81	67
7	24	25	62
9	<17	10	72
06*l*			
0	20	32	0
2	44	39	173
4	101	100	61
6	121	121	23
8	60	52	93
10	37	35	91
07*l*			
1	96	82	264
3	102	106	27
5	29	33	359
7	48	51	74
9	79	61	77
08*l*			
0	81	68	180
2	70	79	271
4	82	86	159
6	37	42	167
8	63	48	87
09*l*			
1	135	125	171
3	154	175	181
5	127	127	173
7	46	42	151
9	23	23	147
0.10.*l*			
0	196	201	180
2	191	206	162
4	135	141	186
6	87	85	184
8	45	39	181
0.11.*l*			
1	180	185	186
3	99	113	159
5	103	87	178
7	29	29	202
0.12.*l*			
0	154	146	180°
2	36	36	176
4	67	70	142
6	35	34	121
0.13.*l*			
1	32	34	86
3	25	22	43
5	43	41	79
7	42	64	78
0.14.*l*			
0	58	53	0
2	36	33	12
4	53	52	33
6	35	46	67
0.15.*l*			
1	20	20	50
3	31	27	4
0.16.*l*			
0	20	30	180
2	<9	7	238
11*l*			
0	325	538	0
2	372	392	29
4	115	117	32
6	93	94	345
8	40	38	282
10	17	14	271
12*l*			
1	174	183	319
3	253	250	7
5	45	49	213
7	175	189	274
9	51	59	275
11	20	32	259
13*l*			
0	304	327	0
2	125	121	166
4	203	223	270
6	187	189	262
8	83	92	272
10	84	83	280
14*l*			
1	107	103	246
3	235	233	229
5	100	102	316
7	101	105	275
9	83	80	303
15*l*			
0	64	53	0
2	51	51	94
4	128	128	335
6	126	126	2
8	45	49	326
10	27	26	324
16*l*			
1	128	129	10
3	225	234	3
5	188	195	6
7	59	56	6
9	47	40	29
17*l*			
0	243	248	0
2	125	117	311
4	159	158	354
6	89	93	4
8	36	42	62
10	17	22	95
18*l*			
1	104	108	244
3	111	121	284
5	21	27	225
7	12	4	76
9	25	28	52
19*l*			
0	133	133	180°
2	133	140	181
4	148	160	231
6	28	44	211
8	33	27	192
1.10.*l*			
1	135	148	178
3	142	161	183
5	56	62	215
7	68	65	209
1.11.*l*			
0	129	138	180
2	83	97	145
4	75	84	151
6	63	66	173
8	8	15	131
1.12.*l*			
1	47	55	146
3	80	73	86
5	105	100	140
7	43	50	90
1.13.*l*			
0	22	25	0
2	57	52	86
4	62	60	111
6	71	66	85
1.14.*l*			
1	39	39	122
3	44	47	80
5	33	34	98
1.15.*l*			
0	90	79	180
2	30	35	126
4	27	31	152
1.16.*l*			
3	25	41	197
21*l*			
1	320	318	163
3	230	228	329
5	104	87	250
7	44	46	2
9	16	18	206
11	7	11	143
22*l*			
0	476	557	180
2	369	358	339
4	148	138	244
6	154	166	242
8	55	57	282
10	40	45	232
23*l*			
1	220	225	290
3	137	132	209
5	157	150	241
7	90	92	266
9	66	65	268
24*l*			
0	78	60	180
2	90	94	98
4	144	154	260
6	57	64	306
8	59	67	311
10	60	56	303
25*l*			
1	73	84	55
3	171	194	2
5	122	116	349
7	116	124	327
9	54	57	328
26*l*			
0	316	300	0°
2	201	209	358
4	198	197	15
6	156	175	341
8	49	59	343
10	<15	13	6
27*l*			
1	214	224	341
3	191	193	355
5	118	112	353
7	36	44	352
9	42	40	6
28*l*			
0	139	123	0
2	118	120	310
4	75	79	302
6	38	38	312
8	24	24	280
29*l*			
1	50	58	260
3	126	136	244
5	71	71	297
7	87	89	253
9	32	43	239
2.10.*l*			
0	<17	19	180
2	105	128	190
4	77	90	272
6	53	64	268
8	39	44	226
2.11.*l*			
1	39	57	234
3	19	14	145
5	22	29	101
7	<21	18	245
2.12.*l*			
0	81	87	0
2	44	46	23
4	61	73	93
6	41	47	69
2.13.*l*			
1	56	72	30
3	70	71	79
5	67	65	65
2.14.*l*			
0	21	19	0
2	66	72	133
4	50	59	99
6	18	34	90
2.15.*l*			
1	53	70	183
3	52	67	158
2.16.*l*			
0	59	68	180
2	45	65	187
31*l*			
0	558	570	180
2	284	276	237
4	124	130	237
6	53	59	195
8	23	30	208
10	50	46	123
32*l*			
1	533	508	219
3	341	314	230
5	195	187	216
7	49	59	241
9	45	42	179
33*l*			
0	375	371	180
2	310	313	207
34*l*			
3	141	109	201°
35*l*			
0	14	36	0
2	220	222	14
36*l*			
3	241	220	32
37*l*			
0	208	192	0
2	141	148	339
38*l*			
3	89	98	325
39*l*			
0	97	82	0
2	50	55	345
3.10.*l*			
3	30	28	259
3.11.*l*			
0	88	83	0
2	81	105	323
3.12.*l*			
3	109	115	356
3.13.*l*			
0	151	130	0
2	44	39	39
3.14.*l*			
3	46	37	98
3.15.*l*			
0	50	40	180
2	44	45	183
41*l*			
1	240	229	144
3	218	211	201
5	141	139	185
7	71	72	193
9	54	47	154
42*l*			
0	611	599	180
2	389	369	215
4	214	201	182
6	187	217	191
8	26	25	157
10	19	16	124
43*l*			
3	289	409	201
44*l*			
0	234	211	180
2	135	129	142
45*l*			
3	145	148	34
46*l*			
0	26	8	0
2	100	94	24
47*l*			
3	38	32	14
48*l*			
0	84	83	180
2	52	55	25
49*l*			
3	31	33	198
4.10.*l*			
0	68	70	0
2	75	93	17

TABLE 5. (*Continued.*)

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
	4.11.*l*		
3	165	166	350°
	4.12.*l*		
0	139	112	0
2	169	176	355
	4.13.*l*		
3	80	85	5
	4.14.*l*		
0	<18	2	0
2	<13	19	351
	4.15.*l*		
3	36	41	269
	4.16.*l*		
0	39	41	180
2	16	25	215
	51*l*		
0	312	330	180
2	65	57	170
4	191	182	175
6	117	110	209
8	37	36	230
10	<13	9	233
	52*l*		
1	250	230	244
3	230	220	170
5	209	215	179
7	78	91	206
9	36	29	157
	53*l*		
0	54	28	0
2	107	119	159
	54*l*		
3	101	101	143
	55*l*		
0	126	105	180
2	76	71	132
	56*l*		
3	109	112	98
	57*l*		
0	93	78	180
2	81	78	172
	58*l*		
3	131	133	187
	59*l*		
0	153	157	180
2	103	121	166
	5.10.*l*		
3	44	41	224
	5.11.*l*		
0	144	109	0
2	146	153	356
	5.12.*l*		
3	113	116	15
	5.13.*l*		
0	73	70	0
2	44	47	19
	5.14.*l*		
2	48	49	289
	5.15.*l*		
0	58	48	180
2	40	45	286

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α
	61*l*		
1	220	226	239°
3	108	104	239
5	96	95	214
7	80	92	272
9	43	40	266
	62*l*		
0	131	79	0
2	136	130	275
4	95	84	197
6	117	138	232
8	31	31	216
10	27	34	263
	63*l*		
3	114	105	114
	64*l*		
0	264	242	0
2	166	182	71
	65*l*		
3	183	178	79
	66*l*		
0	85	69	0
2	91	97	224
	67*l*		
3	159	170	163
	68*l*		
0	265	257	180
2	205	239	175
	69*l*		
3	146	177	176
	6.10.*l*		
0	19	5	0
2	65	81	224
	6.11.*l*		
3	20	18	5
	6.12.*l*		
0	45	40	0
2	18	19	28
	6.13.*l*		
3	16	21	137
	6.14.*l*		
0	<16	4	180
2	31	27	220
	6.15.*l*		
3	19	38	225
	71*l*		
0	20	7	180
2	87	86	299
4	145	171	268
6	60	63	259
8	52	57	272
10	34	59	262
	72*l*		
1	195	180	302
3	165	163	309
5	89	83	279
7	75	95	262
9	42	47	270
	73*l*		
0	236	208	0
2	149	151	41
	74*l*		
3	172	187	9
	75*l*		
0	300	277	0
2	163	180	0

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
	76*l*		
3	68	67	55°
	77*l*		
0	194	179	180
2	154	172	156
	78*l*		
3	142	154	173
	79*l*		
0	95	92	180
2	92	103	191
	7.10.*l*		
3	28	29	170
	7.11.*l*		
0	64	58	180
2	<15	7	191
	7.12.*l*		
3	26	26	100
	7.13.*l*		
0	25	22	180
2	60	66	184
	7.14.*l*		
3	52	64	191
	7.15.*l*		
0	72	70	180
2	14	35	176
	81*l*		
1	44	47	337
3	93	93	310
5	93	100	209
7	57	62	253
9	54	54	260
	82*l*		
0	22	33	0
2	125	121	5
4	114	126	322
6	44	55	256
8	34	37	302
	83*l*		
3	187	202	340
	84*l*		
0	256	236	0
2	209	218	4
	85*l*		
3	227	256	341
	86*l*		
0	22	24	0
2	49	51	3
	87*l*		
3	50	49	233
	88*l*		
0	99	99	180
2	68	77	156
	89*l*		
3	35	31	223
	8.10.*l*		
0	<17	8	0
2	43	44	53
	8.11.*l*		
3	61	60	32
	8.12.*l*		
0	<18	16	180
2	14	21	183

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
	8.13.*l*		
3	57	66	189°
	8.14.*l*		
0	110	104	180
2	64	82	183
	91*l*		
0	112	114	180
2	62	62	196
4	104	113	166
6	75	86	216
8	31	27	233
	92*l*		
1	34	52	302
3	95	105	101
5	25	28	47
7	29	26	285
9	10	11	206
	93*l*		
0	169	149	0
2	118	138	13
	94*l*		
3	156	166	330
	95*l*		
0	126	112	0
2	154	173	305
	96*l*		
3	72	75	317
	97*l*		
0	57	47	180
2	25	29	201
	98*l*		
3	81	72	269
	99*l*		
0	84	67	0
2	49	44	343
	9.10.*l*		
3	85	74	7
	9.11.*l*		
0	103	83	0
2	77	76	20
	9.12.*l*		
3	<14	19	42
	9.13.*l*		
0	17	15	180
2	43	54	179
	10.1.*l*		
1	176	187	189
3	195	223	168
5	36	37	169
7	33	32	175
	10.2.*l*		
0	100	103	180
2	104	108	169
4	87	104	98
6	<22	12	161
8	23	24	91
	10.3.*l*		
3	52	47	122
	10.4.*l*		
0	183	161	0
2	69	78	333
	10.5.*l*		
3	<16	20	86

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
	10.6.*l*		
0	104	99	180°
2	69	79	238
	10.7.*l*		
3	93	86	240
	10.8.*l*		
0	32	29	0
2	44	47	296
	10.9.*l*		
3	80	77	6
	10.10.*l*		
0	116	98	0
2	119	122	6
	10.11.*l*		
3	85	88	359
	10.12.*l*		
0	72	61	0
2	31	27	346
	11.1.*l*		
0	227	229	180
2	141	155	167
4	36	39	146
6	54	53	138
8	18	25	86
	11.2.*l*		
1	91	102	165
3	65	63	157
5	38	44	71
7	42	49	81
	11.3.*l*		
0	<17	23	180
2	25	18	122
	11.4.*l*		
3	56	50	166
	11.5.*l*		
0	93	70	180
2	76	70	185
	11.6.*l*		
3	83	77	178
	11.7.*l*		
0	81	63	180
2	71	63	179
	11.8.*l*		
3	40	34	179
	11.9.*l*		
0	53	48	0
2	68	77	1
	11.10.*l*		
3	92	95	10
	11.11.*l*		
0	79	66	0
2	59	63	353
	12.1.*l*		
1	54	59	176
3	26	25	101
5	15	10	64
7	19	21	17
	12.2.*l*		
0	37	25	180
2	49	44	34
4	28	37	35
6	54	54	72
	12.3.*l*		
3	20	20	338

TABLE 5. (*Continued.*)

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
	12.4.l		
0	82	61	180°
2	60	61	182
	12.5.l		
3	69	65	167
	12.6.l		
0	132	121	180
2	90	90	177
	12.7.l		
3	114	109	177
	12.8.l		
0	<18	7	0
2	46	39	148
	12.9.l		
3	55	50	69
	12.10.l		
0	32	30	0
2	35	41	31
	13.1.l		
0	100	86	0°
2	42	47	30
4	51	49	340
6	46	55	328
	13.2.l		
1	81	102	354
3	75	80	20
5	53	56	37
	13.3.l		
0	89	72	0
2	71	75	19
	13.4.l		
3	21	22	49
	13.5.l		
0	106	88	180
2	58	63	198
	13.6.l		
3	67	63	192
	13.7.l		
0	54	47	180°
2	60	60	162
	13.8.l		
3	41	42	116
	13.9.l		
0	26	16	180
2	40	41	71
	14.1.l		
1	101	107	355
3	61	62	4
5	63	69	354
	14.2.l		
0	141	143	0
2	89	99	14
4	54	65	0
6	23	47	13
	14.3.l		
3	72	81	8
	14.4.l		
0	78	71	0°
2	34	33	35
	14.5.l		
3	<15	9	353
	14.6.l		
0	45	45	180
2	15	17	204
	14.7.l		
3	22	22	255
	14.8.l		
0	<12	5	0
2	25	26	55
	15.1.l		
0	102	88	0
2	51	57	12
4	47	52	11
	15.2.l		
1	76	93	2
3	51	65	359
	15.3.l		
0	78	77	0°
2	48	59	359
	15.4.l		
3	<12	19	355
	15.5.l		
0	24	25	0
2	10	12	267
	15.6.l		
3	19	32	292
	15.7.l		
0	68	72	0
2	13	31	351
	16.1.l		
1	28	36	10
3	14	19	88
	16.2.l		
0	31	30	0
2	25	42	359
	16.4.l		
0	29	20	180
2	18	35	210

to be observed, were not included in the calculation of R but agreement for them is good (see Table 5), only 6 having $|F_c|$ greater than the minimum observable $|F_o|$.

The large discrepancies between observed and calculated structure factors for the very intense 110 and 220 reflexions were attributed to extinction. For 620, $|F_c|$ was considerably less than $|F_o|$ throughout the analysis, the final discrepancy being twice as large as that for any of the other reflexions. The cause of this is thought to be a Renninger double-reflexion effect,[15] which can usually be verified by comparing the intensities of the reflexion in question when it is recorded on two or more photographs taken with different zone axes as the rotation axis. However, in the present case the measured intensity of 620 was considerably larger than the calculated value for both the $hk0$ zero-layer and $2kl$ second-layer equi-inclination photographs. For the former, the double reflexion is from planes $\bar{1}\bar{1}0$ and 730, of which $\bar{1}\bar{1}0$ has the largest intensity in this layer. For the $2kl$ photograph (on which the reflexion $2\bar{6}0$, related by symmetry to 620, is recorded) the double reflexion occurs from $4\bar{4}0$ and $\bar{2}\bar{2}0$ (to produce $2\bar{6}0$). $\bar{2}\bar{2}0$ is a very intense reflexion. The reflexions 110, 220, and 620 were excluded from the final stages of the refinement.

Standard deviations of co-ordinates calculated from equations of the form (Cruickshank *et al.*[13])

$$\sigma^2(x) = [\sum_q (\Delta F_q)^2]/[m - n][\sum_q (\partial |F_q|/\partial x)^2]$$

are given in Table 1. A root-mean-square of $\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ was taken as the standard deviation $\sigma(r)$ of each atomic position. Bond lengths and angles are shown in Table 6 together with their standard deviations calculated from formulæ given by Jeffrey and Cruickshank.[16]

DISCUSSION

In the crystal structure of $P_4N_4(NMe_2)_8$, the molecule has a puckered eight-membered phosphorus–nitrogen ring of symmetry $\bar{4}$ with two sets of crystallographically non-equivalent P–N bonds which are found to be equal in length within experimental error (Table 6). This confirms that there is electron delocalization in the ring as proposed, from different points of view, by Craig [1] and by Dewar *et al.*,[17] but it does not enable us to choose between

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[15] Renninger, *Z. Krist.*, 1937, **97**, 107.

[16] Jeffrey and Cruickshank, *Quart. Rev.*, 1953, **7**, 335.

[17] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

TABLE 6.

Bond lengths (Å) and bond angles with standard deviations (in brackets).

P–N(1)	1·576°	(0·01°)	N(1)–P–N(1′)	120·1°	(0·5°)	P–N(2)–C(1)	114·9°	(0·8°)
P–N(1′)	1·580		N(2)–P–N(3)	103·8		P–N(2)–C(3)	118·6	
P–N(2)	1·686		N(1)–P–N(2)	103·2		P–N(3)–C(2)	125·3	
P–N(3)	1·671		N(1)–P–N(3)	111·8		P–N(3)–C(4)	117·5	
			N(1′)–P–N(2)	113·7				
N(2)–C(1)	1·46	(0·02)	N(1′)–P–N(3)	103·4		C(1)–N(2)–C(3)	116·0	(1·0)
N(2)–C(3)	1·45					C(2)–N(3)–C(4)	115·7	
N(3)–C(2)	1·42		P–N(1′)–P′	133·0	(0·6)			
N(3)–C(4)	1·48							

their alternative theories because both lead to equality of bond lengths in the ring. The lengths found for these P–N bonds, although markedly different from those found by Ketelaar and de Vries[2] in $(PNCl_2)_4$, are similar to those obtained in the more recent structure determinations for $(PNCl_2)_4$ and $P_4N_4Me_8$ (see Table 7) and for $(PNCl_2)_3$ (1·57—1·61 Å).[4] In $(PNF_2)_4$, on the other hand, the P–N bonds are much shorter,[5] 1·49—1·52 Å. Except for $(PNF_2)_4$ the tetrameric compounds so far examined have rings with symmetry $\bar{4}$ but, owing to the flexibility possible with a puckered eight-membered ring, there are minor differences in their shapes. A measure of these differences is provided by the distance of the phosphorus atoms from the mean plane of the ring [(001) plane] in each case, *viz.*, 0·35 Å in $(PNCl_2)_4$ but only 0·18 Å in $P_4N_4(NMe_2)_8$ and 0·21 Å in $P_4N_4Me_8$. A possible explanation for the difference in shape from the chloride is that, if the dimethylamino-groups were attached to a ring shaped as in $(PNCl_2)_4$, there would be steric hindrance between those groups attached to phosphorus atoms at opposite sides of the ring. The flattening of the ring in $P_4N_4(NMe_2)_8$ causes such groups to move farther apart.

TABLE 7.

Comparison of bond lengths and bond angles in the molecules $(PNCl_2)_4$ (Hazekamp *et al.*[3]), $P_4N_4Me_8$ (Dougill[6]), and $P_4N_4(NMe_2)_8$ (this work).

	$(PNCl_2)_4$	$P_4N_4Me_8$	$P_4N_4(NMe_2)_8$
P–N cyclic (Å)	1·569, 1·570	1·591, 1·601	1·576, 1·580
N–P–N cyclic	121·2°	119·8°	120·1°
P–N–P cyclic	131·3	132·0	133·0
Cl–P–Cl exocyclic	102·8		
C–P–C exocyclic		104·1	
N–P–N exocyclic			103·8

In the present structure, the exocyclic bonds P–N(2) and P–N(3), equal in length within experimental error, clearly have a different bond order from the cyclic P–N bonds but are shorter than one would expect for a pure single bond. This shortening may be attributed to two causes: (*a*) the phosphorus atom participates in the formation of π-bonds in the ring, and (*b*) there could be donation of electrons from the lone pair of the exocyclic nitrogen atom into the exocyclic P–N bond, giving the latter some double-bond character. The reduction in the covalent radius of the phosphorus in this compound [effect (*a*)] can be compared with the reduction of the carbon covalent radius leading to a bond shorter than a normal single bond in such a group as $\geqslant C{-}CH_3$, where one C atom is in the sp^2-hybrid state. The covalent radius appropriate to phosphorus in phosphonitrilic compounds can be deduced from the P–C bond length of 1·81 Å found[6] in $P_4N_4Me_8$ since in this compound effect (*b*) cannot be present. Taking the covalent radius of a methyl carbon atom as 0·77 Å and including the Schomaker–Stevenson electronegativity correction, we obtain 1·07 Å for the phosphonitrilic phosphorus radius as compared with 1·10 Å which is quoted as the single-bond radius.[18] For the exocyclic bond in $P_4N_4(NMe_2)_8$, the

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[18] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 3rd edn., 1960, pp. 224—229.

sum of the covalent radii of phosphorus and nitrogen and the electronegativity correction would then be 1·07 + 0·74 − 0·07 = 1·74 Å, as compared with the observed lengths of 1·67 and 1·69 Å. It thus appears that donation from the lone pair of electrons of the nitrogen atom of the dimethylamino-group into the P–N bond [effect (*b*)] causes a further reduction in the bond length. Support for this conclusion comes from the planarity of the $PNMe_2$ groupings. The three bonds at N(3) are very nearly coplanar, the sum of the three bond angles at this atom being 358·5°. At N(2) there is a small deviation from planarity, the sum of the three angles being 349·5°.

In the three tetragonal structures which have been studied, the angles in the ring at the phosphorus and nitrogen atoms, and the angles, Cl–P–Cl, C–P–C, and N(2)–P–N(3), between the exocyclic substituents at the phosphorus are remarkably alike (Table 7). Intermolecular distances in the dimethylamide structure are normal for van der Waals interaction, the shortest $CH_3 \cdots CH_3$ being 3·73, 3·76 Å, and $N \cdots CH_3$ 4·00 Å. Within the molecule, shortest distances between atoms in neighbouring dimethylamino-groups are $CH_3 \cdots CH_3$ 3·54, 3·60, 3·76 Å, and $N \cdots CH_3$ 3·04, 3·11 Å; the cyclic nitrogen is particularly close to two carbon atoms in the same molecule: $N(1) \cdots C(3)$ 2·94 Å and $N(1) \cdots C(2'')$ 2·89 Å.

In this structure the dimethylamide molecules possess four-fold symmetry and will therefore have two equal principal molecular diamagnetic susceptibilities lying in a plane perpendicular to the $\bar{4}$ axis ($K_\perp$) and a third principal molecular susceptibility parallel to this axis ($K_\parallel$). Since all the molecules lie parallel to each other, $K_\perp$ and $K_\parallel$ will be equal respectively to $\chi_\perp$ and $\chi_\parallel$, the principal crystal susceptibilities, and the molecular diamagnetic anisotropy ($K_\parallel - K_\perp$) will be equal to the crystal diamagnetic anisotropy, -5×10^{-6} c.g.s.e.m.u. This value is low in comparison with those found for benzenoid aromatic systems (the molecular anisotropy for the benzene ring is[19] -60×10^{-6} c.g.s.e.m.u.) where a large diamagnetic anisotropy has been considered a direct consequence of the π-electron delocalisation. A low anisotropy has been obtained[20] also for $(PNCl_2)_3$. The apparent contradiction of these results with the view that phosphonitrilic ring compounds have aromatic character (which is supported by measurements of heats of formation[21]) has been dealt with in detail by Craig *et al.*,[20] who find that for $(PNCl_2)_3$ the ring-current contribution to the magnetic anisotropy is actually paramagnetic and that this can be accounted for theoretically. The situation as regards optical birefringence appears to be similar; the value, −0·02, for $P_4N_4(NMe_2)_8$ is numerically much smaller than those for structures involving a parallel arrangement of benzene rings (*e.g.*, hexamethylbenzene, −0·24).

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[19] Hoarau, Lumbroso, and Pacault, *Compt. rend.*, 1956, **242**, 1702.
[20] Craig, Heffernan, Mason, and Paddock, *J.*, 1961, 1376.
[21] Hartley, Paddock, and Searle, *J.*, 1961, 430.