Crystal Structure of Trimeric Phosphonitrilic Bromide

By Edoardo Giglio and Raffaella Puliti

Istituto Chimico, Università di Napoli,
and Centro Nazionale di Chimica delle Macromolecole (CNR) Sez. III, Napoli, Italy

The structure of trimeric phosphonitrilic bromide was refined by three-dimensional differential Fourier synthesis. The crystals are orthorhombic, space group *Pcmn*, with four molecules in a cell with dimensions: $a = 6 \cdot 63 \pm 0 \cdot 01$, $b = 13 \cdot 36 \pm 0 \cdot 02$, $c = 14 \cdot 43 \pm 0 \cdot 02$ Å. The $(PN)_3$ ring is not planar and has a slight chair conformation similar to that found for trimeric phosphonitrilic chloride. No indications were obtained on the equivalence of the PN bond lengths because of the high values of the corresponding standard deviations. Some short intermolecular approaches have been found. The geometry of the molecule is compared with that of other similar compounds.

Introduction

The crystal and molecular structures of several trimeric phosphonitrilic compounds have been investigated in recent years and interesting correlations with their electronic structures have been established (Craig, 1959; Dewar, Lucken & Whitehead, 1960). X-ray diffraction analyses have been carried out on trimeric phosphonitrilic fluoride (Dougill, 1963) and chloride (Cipollini, Pompa & Ripamonti, 1958; Pompa & Ripamonti, 1959; Giglio, 1960; Wilson & Carroll, 1960), on 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (Mani, Ahmed & Barnes, 1965) and on sodium trimetaphosphimate tetrahydrate (Olthof, Migchelsen and Vos, 1965). In order to obtain further information on this class of compound and to examine the influence of substituents on the molecular conformation the structure of trimeric phosphonitrilic bromide (TPB) was undertaken.

A preliminary study on the crystal structure of TPB has previously been reported (Bode, 1949; De Santis, Giglio & Ripamonti, 1962). In this paper the results of a three-dimensional analysis are discussed.

The molecule and the numbering of atoms are shown in Fig. 1.

Experimental

Prismatic crystals, elongated along **a**, suitable for X-ray analysis were prepared by slow evaporation of a solution of TPB in benzene. The X-ray photographs were taken with a crystal enclosed in a sealed thin-walled glass capillary since the compound sublimes slowly at room temperature. From oscillation and precession photographs, taken with Cu $K\alpha$ radiation, the unit-cell parameters were found to be

$$a = 6 \cdot 63 \ (\pm 0 \cdot 01), \ b = 13 \cdot 36 \ (\pm 0 \cdot 02),$$

$$c = 14 \cdot 43 \ (\pm 0 \cdot 02) \ \text{Å}$$

in good agreement with those found by Bode (1949).

The orthorhombic unit cell contains four molecules corresponding to a calculated density of $3 \cdot 18 \ \text{g.cm}^{-3}$.

The lack of a piezoelectric effect and the systematic absences in the reflexions indicate *Pcmn* to be the space group.

Intensity data were collected with Cu $K\alpha$ radiation by means of multiple-film equi-inclination Weissenberg photographs about **a** for layer lines 0 to 3. The zero-layer about the c axis was recorded to provide cross-correlation of the *a*-axis data. Only 538 independent reflexions, which are about 41% of the total, were estimated visually with a set of standard strips.

Care was taken to choose a crystal having approximately cylindrical shape, with a mean cross-section diameter of about 0·25 mm, so as to facilitate the absorption correction (Bradley, 1935). The linear absorption coefficient of TPB is 267 cm⁻¹. Afterwards, the intensities were corrected for Lorentz, polarization and velocity factors and for change of spot shape on upper layer equi-inclination photographs (Phillips, 1954) by a data reduction program written for an IBM 1620 computer (Damiani, De Santis, Giglio & Ripamonti, 1962).

Structure determination

The structure of TPB projected on (100) and (001) had been previously determined (De Santis, Giglio & Ripa-
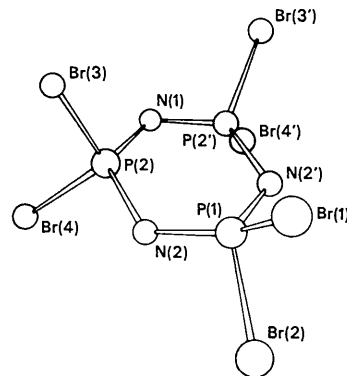

Fig. 1. TPB molecule and atomic numbering.

monti, 1962), giving to the phosphorus and nitrogen atoms the same fractional coordinates as established for trimeric phosphonitrilic chloride because of the very close crystallographic and structural similarity between these two compounds. The coordinates of the bromine atoms were derived from those of the chlorine atoms assuming a P–Br bond length of 2·2 Å. The atomic parameters were then refined by means of two-dimensional Fourier differential synthesis until the reliability indices were $R_{0kl}=0{\cdot}21$ and $R_{hk0}=0{\cdot}17$.

At this stage, starting with the atomic coordinates thus obtained and isotropic temperature parameters, two three-dimensional cycles of structure factors and Fourier synthesis were calculated with programs written for the IBM 1620 computer by Van der Helm (1961*a*, *b*). The *R* index was reduced from 0·40 to 0·26. All the calculations were performed with the atomic scattering factors of McWeeny (1951) for nitrogen atoms and those of James & Brindley (1931) for phosphorus and bromine atoms. The refinement was carried out by means of differential synthesis, calculated with a program written for the IBM 1620 computer (Damiani, De Santis, Giglio & Ripamonti, 1963), which uses output data of Van der Helm's structure-factor program as input data. During the first three cycles individual isotropic temperature factors were assigned and only the positional parameters were adjusted. In the next three cycles individual anisotropic temperature factors were used by comparing observed and calculated curvatures. The *R* index dropped to 0·16.

Since the Weissenberg photographs contained two diagonal lines on which absorption is very large and this phenomenon is due to X-ray surface reflexion fields (Wells, 1937; Buerger, 1938) it was decided to make a rough correction for this effect by multiplying the F_o of the 38 reflexions lying on the diagonal lines by appropriate scale factors. These factors were calculated by averaging the ratios F_c/F_o for each layer. The refinement was then continued until the average shift in the atomic coordinates, in terms of their standard deviations, was less than $0{\cdot}5\sigma$.

The final observed and calculated structure factors are given in Table 1; for these values *R* is 0·132. The final atomic parameters, reported in Table 2 with their estimated standard deviations (Cruickshank, 1949), do not differ appreciably from those obtained before the last correction. The lower accuracy of the *x* co-

Table 1. *Comparison between final observed and calculated structure factors*

Values are multiplied by 10.

H	K	L	FO	FC
0	0	2	434	237
0	0	4	2543	-2510
0	0	6	486	-485
0	0	8	1691	-1678
0	0	10	1260	1227
0	0	12	682	581
0	0	14	240	-260
0	0	16	92	106
0	0	18	55	-37
0	2	0	98	-90
0	4	0	1717	1693
0	6	0	2939	-2903
0	8	0	173	-132
0	10	0	2182	-1942
0	12	0	396	354
0	16	0	185	151
0	1	2	92	-73
0	2	2	407	-409
0	3	2	5248	-5185
0	4	2	1142	-1399
0	5	2	249	-338
0	6	2	214	231
0	7	2	1737	-1731
0	8	2	130	150
0	9	2	549	582
0	10	2	185	179
0	11	2	234	246
0	12	2	280	261
0	13	2	616	559
0	14	2	228	223
0	15	2	127	-131
0	17	2	66	52
0	1	4	754	-735
0	2	4	165	143
0	3	4	107	-60
0	4	4	578	-549
0	5	4	647	782
0	6	4	905	985
0	7	4	861	820
0	9	4	306	314
0	10	4	460	459
0	11	4	280	284
0	12	4	124	-150
0	15	4	324	-248
0	1	6	277	284
0	2	6	298	320
0	3	6	855	-790
0	4	6	731	758
0	5	6	381	-427
0	6	6	283	334
0	7	6	335	-504
0	9	6	176	183
0	10	6	84	-115
0	12	6	338	-320
0	13	6	185	138
0	14	6	355	-220
0	15	6	38	33
0	1	8	168	167
0	2	8	708	-708
0	3	8	1032	948
0	4	8	462	-523
0	5	8	465	-497
0	6	8	708	744
0	7	8	58	97
0	8	8	353	356
0	9	8	173	-169
0	10	8	457	435
0	11	8	199	-152
0	13	8	156	-102
0	14	8	64	56
0	15	8	225	143
0	1	10	376	371
0	2	10	145	-129
0	3	10	1144	1081
0	5	10	353	452
0	6	10	214	-227
0	7	10	332	408
0	10	10	338	-324
0	11	10	133	-136
0	12	10	46	46
0	13	10	260	-169
0	14	10	121	60
0	1	12	142	99
0	2	12	436	418
0	3	12	592	-539
0	4	12	205	-290
0	7	12	347	-323
0	8	12	208	-216
0	10	12	194	-135
0	12	12	49	-27
0	13	12	130	95
0	1	14	309	-321
0	4	14	159	-169
0	5	14	81	-89
0	6	14	52	74
0	7	14	69	112
0	9	14	173	-92
0	10	14	156	103
0	11	14	156	108
0	1	16	84	-66
0	2	16	52	-42
0	4	16	191	172
0	6	16	124	-111
0	7	16	87	67
0	1	18	46	33
0	3	18	52	-52
0	4	18	29	31
1	0	1	983	-941
1	0	2	1133	1312
1	0	3	1601	1729
1	0	4	3378	3665
1	0	5	2454	-2667
1	0	6	1087	-1059
1	0	8	1433	-1109
1	0	9	879	700
1	0	10	121	143
1	0	11	618	-507
1	0	12	347	-252
1	0	13	225	174
1	0	14	202	178
1	0	15	69	-48
1	0	16	98	69
1	0	17	95	-54
1	0	18	61	-53
1	3	0	801	760
1	5	0	405	-349
1	7	0	520	-521
1	9	0	728	-588
1	11	0	254	-208
1	15	0	220	183
1	17	0	72	83
1	1	1	332	226
1	2	1	572	588
1	3	1	1130	1036
1	4	1	234	269
1	5	1	156	134
1	6	1	954	-830
1	7	1	1020	863
1	8	1	549	-468
1	9	1	422	327
1	10	1	656	557
1	12	1	121	101
1	13	1	272	-246
1	16	1	46	33
1	17	1	81	-73
1	1	2	92	-86
1	2	2	662	-579
1	3	2	2127	2102
1	4	2	301	-319
1	5	2	590	691
1	6	2	827	-744
1	7	2	653	725
1	8	2	107	124
1	9	2	436	-344
1	11	2	110	-74
1	12	2	462	347
1	13	2	298	-224
1	14	2	153	140
1	1	3	1130	873
1	2	3	1003	804
1	3	3	2139	-1817
1	4	3	905	845
1	5	3	618	-849
1	6	3	644	-623
1	7	3	457	-470
1	8	3	361	-352
1	9	3	801	758
1	10	3	613	-474
1	12	3	150	-126
1	13	3	81	58
1	14	3	104	-85
1	15	3	66	74
1	16	3	38	51
1	2	4	1035	867
1	3	4	1113	-936
1	4	4	610	606
1	5	4	211	275
1	6	4	1162	-1315
1	7	4	84	-127
1	8	4	471	-473
1	9	4	234	210
1	10	4	763	-700
1	11	4	116	99
1	12	4	101	83
1	13	4	75	67
1	15	4	64	-77
1	16	4	92	78
1	1	5	691	-649
1	2	5	133	-181
1	3	5	616	-551
1	4	5	1263	-1288
1	5	5	1142	-1084
1	6	5	1260	1473
1	7	5	75	-99
1	8	5	205	273
1	10	5	488	423
1	11	5	171	187
1	12	5	92	-86
1	14	5	142	139
1	15	5	124	96
1	16	5	127	-105
1	1	6	376	-370
1	2	6	234	169
1	3	6	2017	-2128
1	4	6	448	-504
1	5	6	497	-556
1	6	6	329	370
1	7	6	725	-669
1	9	6	234	271
1	10	6	425	279
1	11	6	335	194
1	13	6	289	246
1	1	7	1202	-965
1	2	7	708	-688
1	3	7	2026	1696
1	4	7	289	346
1	5	7	335	350
1	7	7	893	876
1	8	7	373	414
1	9	7	575	-518
1	10	7	231	-199
1	11	7	202	188
1	13	7	205	-194
1	1	8	298	-316
1	2	8	428	-379
1	3	8	379	362
1	6	8	315	384
1	7	8	384	399
1	8	8	234	231
1	10	8	182	188
1	11	8	66	82
1	13	8	75	-73
1	14	8	46	-64
1	15	8	64	-61
1	1	9	156	181
1	2	9	162	-135
1	3	9	497	-424
1	4	9	815	730
1	5	9	460	465
1	6	9	451	-554
1	7	9	431	-439
1	9	9	113	-147
1	10	9	162	-196
1	13	9	197	140
1	14	9	194	-113
1	1	10	107	122
1	2	10	81	-51
1	4	10	344	327
1	10	10	92	-131
1	12	10	90	-82
1	14	10	90	-68
1	1	11	173	181
1	5	11	153	148
1	6	11	139	-163
1	7	11	84	-97
1	10	11	257	244
1	11	11	87	-57
1	12	11	84	71
1	1	12	156	111
1	2	12	124	-119
1	3	12	121	103
1	4	12	130	-150
1	6	12	116	129
1	7	12	66	-71
1	8	12	52	62
1	10	12	101	90
1	12	12	72	15
1	1	13	220	223
1	2	13	182	147
1	4	13	92	106
1	5	13	66	60
1	6	13	147	-162
1	8	13	92	-96
1	9	13	159	141
1	11	13	55	-61
1	1	14	55	68
1	2	14	46	65
1	3	14	188	148
1	4	14	46	-44
1	5	14	113	171
1	6	14	43	-44
1	7	14	40	64
1	8	14	38	-41
1	9	14	52	-9
1	10	14	32	-34
1	2	15	168	138
1	3	15	194	-167
1	4	15	130	-138
1	5	15	118	-127
1	6	15	118	107
1	7	15	90	-84
1	8	15	78	-65
1	9	15	78	61
1	1	16	46	-42
1	2	16	101	108
1	3	16	92	-89
1	6	16	38	-11
1	8	16	61	-60
1	1	17	92	-79
1	2	17	61	-51
1	3	17	64	55
1	4	17	43	-56
1	6	17	55	61
1	1	18	52	-62
1	2	18	55	-22
2	0	1	3297	3625
2	0	2	373	-159
2	0	3	1023	805
2	0	4	194	-153
2	0	5	931	-813
2	0	6	329	274
2	0	7	694	613
2	0	8	176	-108
2	0	9	1243	-1230
2	0	10	396	300
2	0	11	136	155
2	0	13	419	375
2	0	14	81	-82
2	0	15	171	-165
2	0	16	52	21
2	2	0	1301	-1512
2	4	0	384	411
2	6	0	257	80
2	8	0	1003	781
2	10	0	584	-567
2	12	0	107	99
2	14	0	40	-24
2	16	0	23	-6
2	1	1	87	57
2	2	1	772	928
2	3	1	2474	2626
2	4	1	1578	1318
2	5	1	997	1013
2	6	1	1604	-1574
2	7	1	616	664
2	8	1	647	-569
2	9	1	552	-592
2	10	1	991	-678
2	11	1	159	-179
2	13	1	150	-172
2	14	1	58	-99
2	16	1	118	98
2	1	2	682	433
2	2	2	396	-199
2	3	2	381	-370
2	4	2	407	-433
2	5	2	1194	1041
2	6	2	448	500
2	7	2	355	-423
2	8	2	171	163
2	9	2	133	-148
2	11	2	173	-104
2	14	2	46	50
2	15	2	101	-90
2	1	3	1179	1065
2	2	3	887	690
2	3	3	2381	-2271
2	5	3	445	-484
2	6	3	971	-968
2	7	3	1222	-1321
2	8	3	445	-552
2	9	3	335	350
2	10	3	246	257
2	11	3	165	-195
2	12	3	142	154
2	13	3	306	317
2	1	4	171	-219
2	2	4	448	389
2	3	4	691	512
2	5	4	526	493
2	6	4	107	-98
2	7	4	116	100
2	8	4	194	-223
2	9	4	176	-304
2	15	4	32	-46
2	1	5	376	332
2	2	5	327	296
2	4	5	818	-663
2	5	5	87	-165
2	7	5	512	561
2	8	5	171	-208
2	9	5	436	569
2	10	5	384	405
2	12	5	75	76
2	13	5	145	-164
2	14	5	139	111
2	1	6	434	331
2	2	6	353	309
2	3	6	260	-200
2	4	6	197	193
2	6	6	393	-402
2	7	6	118	-145
2	8	6	217	-231
2	9	6	156	153
2	11	6	101	-96
2	1	7	237	-194
2	2	7	786	639
2	3	7	772	-561
2	5	7	815	-766
2	6	7	153	228
2	8	7	231	-227
2	9	7	234	271
2	10	7	280	-342
2	11	7	162	132
2	12	7	205	-213
2	2	8	228	221
2	3	8	90	1
2	4	8	292	-250
2	5	8	436	-468
2	6	8	81	106
2	7	8	58	80
2	8	8	133	-127
2	9	8	84	162
2	10	8	52	80
2	1	9	546	-564
2	2	9	405	-419
2	4	9	367	-424
2	5	9	558	-642
2	6	9	604	725
2	8	9	318	300
2	9	9	159	-220
2	10	9	182	221
2	11	9	104	147
2	14	9	58	38
2	2	10	199	-213
2	5	10	243	-215
2	8	10	101	138
2	10	10	113	-130
2	1	11	127	-90
2	2	11	581	-497
2	3	11	763	772
2	4	11	269	352
2	5	11	280	366
2	6	11	145	-152
2	7	11	341	345
2	8	11	217	264
2	9	11	121	-185
2	10	11	66	-89
2	13	11	61	-97
2	3	12	153	-137
2	4	12	104	-129
2	5	12	58	116
2	6	12	118	158
2	7	12	78	-74
2	1	13	208	241
2	3	13	162	-176
2	4	13	228	250
2	5	13	142	155
2	6	13	173	-261
2	7	13	147	-196
2	10	13	139	-98
2	11	13	66	-74
2	3	14	90	75
2	9	14	87	-85
2	4	15	38	-78
2	7	16	55	9
3	0	2	509	440
3	0	3	838	-674
3	0	4	2581	2688
3	0	5	1760	1770
3	0	6	1214	-1092
3	0	7	780	681
3	0	8	795	-716
3	0	9	428	-421
3	0	10	295	354
3	0	11	133	-172
3	0	12	150	-242
3	0	13	98	-203
3	0	14	133	144
3	3	0	217	-278
3	5	0	905	-978
3	7	0	486	-403
3	15	0	162	166
3	2	1	150	-208
3	3	1	202	253
3	4	1	225	433
3	5	1	347	-473
3	6	1	480	521
3	8	1	185	174
3	9	1	173	-250
3	12	1	168	-193
3	14	1	104	-157
3	1	2	561	-626
3	2	2	1036	-1074
3	3	2	1483	1494
3	4	2	156	-214
3	7	2	624	790
3	8	2	468	520
3	9	2	249	-280
3	12	2	231	243
3	13	2	150	-232
3	1	3	702	689
3	2	3	766	-743
3	3	3	1694	1497
3	5	3	306	513
3	8	3	272	352
3	9	3	254	-220
3	10	3	156	197
3	11	3	260	-305
3	2	4	410	-230
3	3	4	798	-570
3	4	4	873	823
3	5	4	647	710
3	6	4	532	-858
3	10	4	711	-773
3	15	4	58	-94
3	1	5	624	489
3	2	5	867	757
3	3	5	728	660
3	5	5	595	587
3	6	5	434	-554
3	8	5	225	-421
3	10	5	173	-339
3	11	5	133	-172
3	2	6	220	329
3	3	6	1867	-1498
3	4	6	497	-515
3	5	6	353	288
3	6	6	324	391
3	7	6	477	-734
3	10	6	214	314
3	13	6	156	257
3	1	7	243	-301
3	2	7	376	329
3	3	7	1052	-834
3	5	7	237	-343
3	6	7	225	-278
3	13	7	87	118
3	1	8	312	-324
3	3	8	728	562
3	7	8	191	385
3	1	9	185	-219
3	3	9	295	-291
3	1	10	156	185
3	4	10	312	325
3	11	10	81	-75
3	1	11	139	-122
3	4	12	156	-233

ordinates must be ascribed to the lack of reflexions of layer lines with $h > 3$. Furthermore the low percentage of the reflexions used in the refinement and the absorption effect, approximately corrected, do not allow one to attach any physical meaning to the numerical values of anisotropic thermal parameters, listed in Table 3. The comparison between observed and calculated peak heights is given in Table 4. The e.s.d.'s of the electron density and of its first derivatives are: $\sigma(\varrho) = 0.40$ e.Å^{-3}; $\sigma(A_h) = 0.78$, $\sigma(A_k) = 1.04$, $\sigma(A_l) = 0.92$ e.Å^{-4}.

Table 2. Final fractional atomic coordinates

(e.s.d.'s × 10³ Å)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
N(1)	0.591_3	60	0.250_0	—	0.136_3	33
N(2)	0.428_7	59	0.147_3	30	-0.003_3	37
P(1)	0.410_5	16	0.250_0	—	-0.059_5	7
P(2)	0.553_4	19	0.146_5	7	0.091_6	8
Br(1)	0.580_7	8	0.250_0	—	-0.190_0	4
Br(2)	0.101_5	9	0.250_0	—	-0.108_9	5
Br(3)	0.847_7	10	0.071_6	5	0.083_0	5
Br(4)	0.381_8	9	0.050_3	4	0.180_4	4

Table 3. Final temperature factors

Temperature factor $= \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2)\right]$

	b_{11}	b_{22}	b_{33}
N(1)	0.02691	0.00600	0.00927
N(2)	0.02521	0.00720	0.00865
P(1)	0.01538	0.00720	0.00650
P(2)	0.02291	0.00590	0.00713
Br(1)	0.03108	0.00958	0.00852
Br(2)	0.02982	0.01150	0.00972
Br(3)	0.02975	0.01060	0.01100
Br(4)	0.03125	0.00900	0.00915

The intramolecular distances and angles with their standard deviations, estimated with the Ahmed & Cruickshank (1953) and Darlow (1960) formulae, are shown in Table 5. A view of the arrangement of the molecules in the crystal, showing the closest intermolecular contacts less than the normal van der Waals distances, is shown in Fig. 2.

Discussion

The most interesting feature of the structure lies in the geometry of the molecule. The equation of the ring least-squares plane, calculated according to Schomaker, Waser, Marsh & Bergman (1959) and using unitary weights for all the atoms, is:
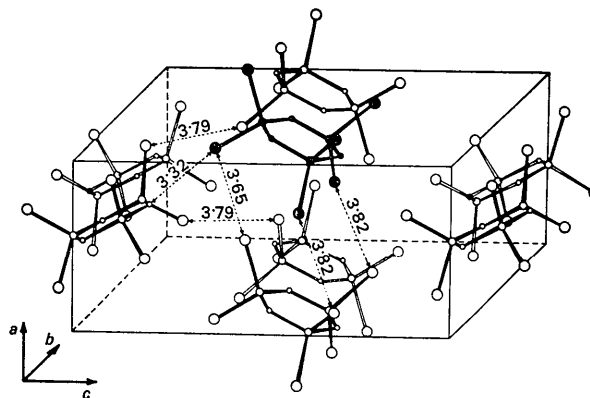
Fig. 2. Drawing of the unit cell showing the molecular packing and the closest intermolecular approaches.

Table 4. Electron densities and curvatures

Values in parentheses are from F_c differential synthesis.

		ϱ e.Å^{-3}	$-A_{hh}$ e.Å^{-5}	$-A_{kk}$ e.Å^{-5}	$-A_{ll}$ e.Å^{-5}	A_{hk} e.Å^{-5}	A_{hl} e.Å^{-5}	A_{kl} e.Å^{-5}
N(1)	Obs.	4.94	12.8	31.7	27.4	—	-2.4	—
	Calc.	(5.29)	(16.6)	(30.5)	(29.7)	—	(0.0)	—
N(2)		5.11	13.3	34.5	25.2	2.1	-3.8	-6.4
		(5.06)	(13.3)	(34.0)	(25.6)	(2.4)	(-1.4)	(-4.7)
P(1)		15.79	49.2	138.9	130.4	—	-13.1	—
		(15.86)	(50.8)	(139.5)	(129.2)	—	(-12.6)	—
P(2)		15.20	42.1	147.3	113.6	3.9	0.3	4.2
		(15.10)	(42.7)	(145.3)	(113.9)	(2.3)	(1.4)	(4.5)
Br(1)		32.95	93.8	241.5	242.6	—	3.9	—
		(32.71)	(96.8)	(241.2)	(241.5)	—	(3.7)	—
Br(2)		30.89	90.1	212.4	203.3	—	-6.6	—
		(29.91)	(89.0)	(211.3)	(202.4)	—	(-5.0)	—
Br(3)		28.70	80.8	202.7	175.6	3.5	4.3	-3.2
		(28.71)	(82.7)	(201.2)	(176.3)	(0.1)	(1.3)	(-1.4)
Br(4)		32.55	91.6	263.7	218.8	-5.0	4.9	13.7
		(32.57)	(95.4)	(259.7)	(217.2)	(-2.8)	(2.4)	(5.5)

Table 5. Bond lengths and angles with their standard deviations

	l	$\sigma(l)$		θ	$\sigma(\theta)$
N(1)P(2)	1.55 Å	0.035 Å	P(2)N(1)P(2')	126.8°	2.6°
N(2)P(1)	1.60	0.033	P(2)N(2)P(1)	118.6	2.4
N(2)P(2)	1.60	0.045	N(2)P(1)N(2')	118.3	1.8
P(1)Br(1)	2.20	0.011	N(1)P(2)N(2)	115.8	2.0
P(1)Br(2)	2.17	0.017	Br(1)P(1)Br(2)	101.7	0.4
P(2)Br(3)	2.20	0.019	Br(3)P(2)Br(4)	103.4	0.4
P(2)Br(4)	2.14	0.013			

$$2 \cdot 2227x - 2 \cdot 3384z = 1 .$$

These coefficients are referred to the crystallographic axes and x and z are fractional coordinates. The distance of this plane from the origin of the unit cell is 2·69 Å. The deviations of the atoms from the plane are in Å:

N(1), −0·012; N(2), −0·106; P(1), 0·138; P(2), 0·043 .

Therefore the (PN)₃ ring in the TPB molecule has a slight chair conformation and deviates from planarity appreciably more than in the hexachloro (Giglio, 1960) and in the diphenyltetrachloro (Mani, Ahmed & Barnes, 1965) derivative, in which the average distances of P and N atoms from the least-squares plane are 0·037 and 0·042 Å respectively. Since the ring is planar in the hexafluoro derivative (Dougill, 1963) it seems reasonable to think that the deviation from planarity increases on lowering the degree of electronegativity of the ligands and at the same time the aromaticity decreases.

Unfortunately only rough indications have been obtained of the PN bond lengths of TPB because of the high values of the corresponding standard deviations, and the equivalence of these bonds cannot be established or excluded. However, the mean values of the PN bonds seem to increase from the hexafluoro and hexachloro compounds (1·56 Å) to the diphenyltetrachloro and hexabromo derivatives (1·58 Å) and this should cause a loss of aromaticity. These results are in qualitative agreement with the theoretical expectation that the bond strength should be greater if the electronegativity of the ligand increases (Paddock, 1964). Another noticeable effect might be the progressive departure from regular tetrahedral hybridization of the phosphorus orbitals when the ligands are less electronegative.

To show the situation in TPB some values of the bond angles in the two crystallographically non-equivalent PNBr₂ units of the molecule are shown in Fig. 3. Moreover, the distances of Br(1) and Br(2) from the plane N(2)P(1)N(2′) and those of Br(3) and Br(4) from the plane N(1)P(2)N(2) are 1·39, −1·92 Å and 1·64, −1·74 Å respectively. These values show a
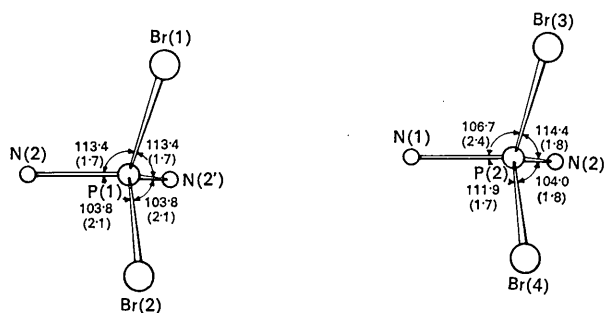
considerable deviation from regular tetrahedral geometry and a probable smaller conjugation between the ring and the exocyclic π-systems.

It might be also noted that, on the average, the bond angles on the nitrogen atoms of the (PN)₃ rings are larger, although not always significantly, than those on the phosphorus atoms in all the compounds of the series thus far studied, except in the case of trimeric phosphonitrilic chloride investigated by Wilson & Carroll (1960).

Finally it should be mentioned that the shorter intermolecular approaches (Fig. 2) occur mainly in directions approximately parallel to the a axis and correspond to the shortest contacts in the hexachloro derivative. This situation is confirmed by inspection of the anisotropic thermal parameters, which show that, generally, the atoms present directions of maximum and minimum vibration respectively along the c and a axes.

Fig. 3. Some bond angles and their standard deviations (°) in the two crystallographically non-equivalent PNBr₂ units of the TPB molecule.

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