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The Crystal and Molecular Structure of 1,1-Bis(dimethylamino)-2,4,6-triphenylphosphorin

By Ulf Thewalt
Mineralogisches Institut der Universität, 355 *Marburg, Germany*

and Charles E. Bugg
Institute of Dental Research and Laboratory of Molecular Biology, University of Alabama in Birmingham, Birmingham, Alabama 35233, *U.S.A.*

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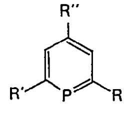
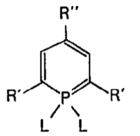
1,1-Bis(dimethylamino)-2,4,6-triphenylphosphorin, $C_{27}H_{29}PN_2$, crystallizes in the orthorhombic space group *Pbca* with $a=13{\cdot}993$, $b=15{\cdot}657$, and $c=21{\cdot}624$ Å; there are eight formula units in the cell. The structure was determined by the symbolic addition procedure and refined by three-dimensional least-squares calculations. The final conventional R index is 0·091 for 3932 reflections. The coordinating ligands about the phosphorus atom form a distorted tetrahedron with P–N and P–C distances of 1·66 and 1·74 Å respectively. The PC_5 ring is essentially planar. The molecular geometry indicates a delocalized 6π electron system.

Introduction

Phosphorins are heterocyclic phosphorus compounds with structure formulas (I) and (II).



(I)



(II)

R, R', R''=alkyl or aryl

L=R, OR, NR_2

A number of phosphorins have been synthesized recently by Dimroth, Hettche, Städe & Steuber (1969) and by Märkl (1968). As evidenced by chemical and spectroscopic data, the PC_5 ring of the phosphorins is an aromatic system with the phosphorus atom participating in π-bonding. Though π-bonding properties of phosphorus are of considerable current interest, there is little agreement about the proper theoretical description of the π-bonding that occurs in phosphorus compounds. On the other hand, π-bonding in certain aromatic heterocyclic compounds, such as pyridine, is relatively well understood. Since the PC_5 ring of phosphorins is an analog of pyridine, the phosphorins are good model systems for studying the π-bonding properties of phosphorus when it is incorporated as part of a familiar aromatic system.

A necessary prerequisite for a detailed analysis of the bonding in phosphorins is the knowledge of their exact geometries, particularly the configurations around the phosphorus atoms. Crystallographic studies of some phosphorins have been reported (Bart & Daly, 1968; Fischer, Hellner, Chatzidakis & Dimroth, 1968; Daly & Märkl, 1969; Thewalt, 1969; Daly, 1970). In this paper we report the crystal and molecular structure of 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin (Fig. 1). A preliminary report of this work has been published (Thewalt, Bugg & Hettche, 1970).

Experimental

A sample of 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin was generously supplied by Professor K. Dimroth. The compound was crystallized as yellow, fluorescing plates by slowly evaporating an ethanol solution at room temperature. Weissenberg photographs showed that the crystals are orthorhombic. The space group *Pbca* was indicated by the following systematic absences of reflections: $0kl$ absent when k is odd; $h0l$ absent when l is odd; and $hk0$ absent when h is odd. The crystal used for the determination of lattice constants and for the collection of intensity data was cut from a larger crystal and had dimensions 0·32, 0·25, 0·12 mm in the directions parallel to **a**, **b** and **c**, respectively.

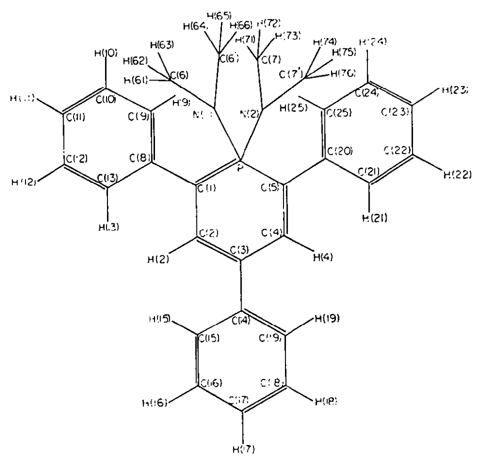


Fig. 1. Structural formula and numbering scheme for 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin.

The crystal was mounted on a Picker FACS-1 diffractometer with **b** parallel to the φ axis of the diffractometer. The 2θ values for 17 high angle reflections (Cu $K\alpha_1$, $\lambda = 1{\cdot}54051$ Å) were measured; the cell dimensions were determined by a least-squares analysis which minimized the differences between observed and calculated 2θ values. The density of the crystals was measured by flotation in an aqueous sodium bromide solution. Crystal data are listed in Table 1.

Table 1. *Crystal data for 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin*

$C_{27}H_{29}PN_2$
Space group *Pbca*
$a = 13{\cdot}993$ (1) Å
$b = 15{\cdot}657$ (2)
$c = 21{\cdot}624$ (2)
$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å

M.W. 412·5
$Z = 8$
$D_m = 1{\cdot}16$ (1) g.cm^{-3}
$D_x = 1{\cdot}155$ g.cm^{-3}
$F(000) = 1760$

Intensity values were measured with the diffractometer, using nickel-filtered copper radiation, a scintillation detector, and a θ–2θ scanning technique. A scan speed of 1 °/min was used, and the background was counted for 20 seconds at each terminus of the scans. The 3932 unique reflections in the range $4° \leq 2\theta \leq 128°$ were measured. The intensity values were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts, as well as an additional term $(0{\cdot}03S)^2$, S being the scan counts. The data were corrected for geometric factors. Absorption corrections were applied, using a modified version of the computer program *ORABS* (Wehe, Busing & Levy, 1962). By means of a K curve (Karle & Hauptman, 1953), the structure amplitudes, $|F|$, were placed on an approximately absolute scale and normalized structure factor magnitudes, $|E|$, were derived. The statistical distribution of E values, with the theoretical values for centrosymmetric space groups given in parentheses, are:

$$\langle |E| \rangle = 0{\cdot}817\ (0{\cdot}798)$$
$$\langle |E|^2 \rangle = 0.997\ (1{\cdot}00)$$
$$\langle |E^2 - 1| \rangle = 0{\cdot}915\ (0{\cdot}968).$$

Determination and refinement of the structure

Using a computer program, the structure was solved by the symbolic addition procedure for centrosymmetric space groups (Karle & Karle, 1966). The origin was specified by the assignments: $S(7,1,14) = S(1,2,1) = S(5,4,14) = -$, where S means 'sign of'. Phases for two additional reflections, 5,2,5 and 12,6,3, were assigned the symbols a and b, respectively. These five starting reflections had large E values and were involved in a relatively large number of $\sum_2$ interactions. Beginning with this set of reflections and considering first only reflections with $E \geq 2{\cdot}8$, phases or symbols were assigned to additional reflections by iterative application of the $\sum_2$ formula. Additional reflections were added by lowering the E limit between successive cycles. In the presence of numerous supporting indications, with no (or in later cycles, relatively few) contraindications, a new phase assignment was automatically accepted. Following this procedure, the set of phase assignments was continuously expanded until all reflections with $E \geq 1{\cdot}8$ were included. During the final cycles, it became obvious that a was $-$ and b was $+$. An E map, calculated by using the final set of phases, clearly revealed the positions of the nonhydrogen atoms, although some of the carbon atoms of the phenyl groups were represented by weak peaks. A few spurious peaks were also present in the E map, but these did not seriously complicate efforts to obtain the trial structure.

The trial structure was refined by least-squares, using the complete set of three-dimensional data. The diagonal approximation was used in the early stages of refinement. The block-diagonal approximation was used in the later stages. The quantity minimized was $\sum w(|F_o| - |F_c|/k)^2$ where k is a scale factor and w is equal to $\{2|F_o|/\sigma(F_o^2)\}^2$. Atomic scattering factors for P, N, and C were taken from *International Tables for X-ray Crystallography* (1962), and those for H were from Stewart, Davidson & Simpson (1965). Initially, the heavy atom positional and isotropic temperature parameters were refined to an R index $(\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·163. Subsequent anisotropic refinement lowered R to 0·133. At this stage the 29 hydrogen atoms were easily located in a difference Fourier synthesis. Assuming that all hydrogen atoms had isotropic temperature factors of 3·0 Å^2 and keeping the hydrogen parameters fixed, further refinement resulted in an R index of 0·113. At this stage, the agreement between observed and calculated structure factors was generally consistent with the estimated errors in the values of F_o, but we noticed that nine reflections showed discrepancies greatly exceeding their estimated errors. It is possible that these reflections were affected by extinction, but it is more likely that they were incorrectly measured. These nine reflections were assigned zero weights. Finally, all positional parameters were refined along with anisotropic temperature parameters for the heavy atoms and isotropic temperature parameters for

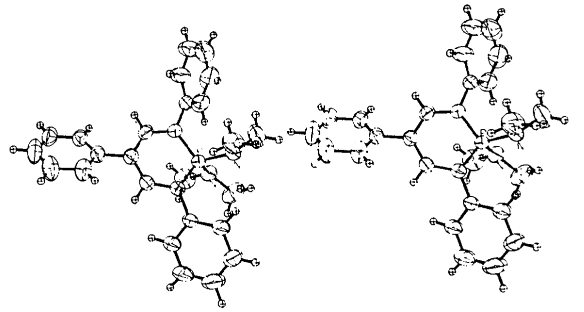


Fig. 2. A stereoscopic view of the molecule. The heavy atoms are represented by ellipsoids defined by the principal axes of the thermal vibration and scaled to include 50% probability. The hydrogen atoms are represented by spheres of 0·1 Å radius. This drawing was prepared using the computer program *ORTEP* (Johnson, 1965).

Table 2. *Observed and calculated structure factors*

From left to right, the columns contain values of l, $10F_o$, and $10F_c$. An asterisk indicates that the reflection was given zero weight in the least-squares calculations.

0	0	L
2	1740	1849
4	2775	-3152*
6	862	-857
8	819	812
10	539	-517
12	524	-490
14	187	172
16	575	-576
18	251	-254
20	275	278
22	139	149
24	117	115
0	2	L
0	735	-753
1	729	-735
2	128	35*
3	2843	-3145*
4	753	745
5	1029	-1051
6	107	-103
7	43	46
8	227	238
9	1221	1219
10	194	-184
11	69	21
12	224	-228
13	157	-164
14	167	-159
15	110	-120
16	78	-92
17	225	231
18	158	174
19	445	464
20	81	50
21	249	258
22	127	-147
23	183	-173
24	77	-88
25	119	-125
0	4	L
0	2238	-2345
1	236	-241
2	2300	-2447
3	54	-74
4	2328	-2446
5	181	177
6	1322	1341
7	243	-243
8	1041	1026
9	290	-281
10	223	-224
11	163	-156
12	234	-240
13	190	195
14	393	401
15	96	-105
16	463	464
17	97	95
18	71	78
19	68	67
20	284	-297
21	235	-244
22	78	-66
23	49	14
24	52	-37
0	6	L
0	466	-461
1	76	73
2	331	311
3	358	356
4	195	-184
5	798	806
6	802	-750
7	320	306
8	151	-137
9	768	-767
10	667	637
11	184	-179
12	429	418
13	200	214
14	118	118
15	586	601
16	97	-54
17	441	-445
18	91	-75
19	315	-307
20	53	77
21	76	-73
22	172	160
23	110	87
0	8	L
0	430	446
1	155	147
2	714	710
3	581	-586
4	169	149
5	452	-447
6	330	-318
7	598	623
8	309	294
9	519	502
10	93	77
11	125	115
12	93	-61
13	366	-396
14	386	-408
15	0	2
16	131	124
17	116	110
18	102	-92
19	105	106
20	35	-7
21	10	-5
22	121	115
0	10	L
0	202	-199
1	140	-148
2	80	21
3	67	-87
4	391	383
5	211	205
6	166	157
7	114	102
8	103	-111
9	102	127
10	161	-162
11	218	-220
12	297	-301
13	189	-177
14	147	-148
15	275	-268
16	123	137
17	98	67
18	104	-67
19	90	82
20	66	-86
21	151	145
0	12	L
0	294	-290
1	351	358
2	90	-47
3	444	450
4	269	284
5	127	-132
6	312	307
7	280	-287
8	147	-173
9	115	-83
10	243	-273
11	87	-60
12	136	-109
13	83	33
14	175	177
15	33	16
16	64	24
17	45	31
18	77	66
19	148	-149
0	14	L
0	176	186
1	99	-84
2	94	62
3	59	28
4	179	-191
5	106	-89
6	133	-111
7	142	-132
8	88	-52
9	87	-71
10	119	130
11	109	86
12	259	249
13	213	224
14	34	38
15	180	201
16	96	-89
0	16	L
0	74	31
1	144	-143
2	94	-100
3	121	-130
4	122	-124
5	72	-42
6	93	-95
7	78	83
8	52	4
9	120	140
10	54	44
11	67	50
12	131	131
0	18	L
0	82	-84
1	26	46
2	104	-104
3	54	-25
4	68	63
1	0	L
2	1125	-1180
4	532	-526
6	335	352
8	684	706
10	373	359
12	488	-478
14	73	48
16	72	44
18	268	262
20	359	375
22	71	-4
24	195	-202
1	1	L
1	685	685
2	758	-776
3	902	-905
4	403	-392
5	412	410
6	772	785
7	322	-326
8	602	585
9	59	57
10	676	649
11	204	-192
12	160	142
13	411	393
14	41	-25
15	66	64
16	111	-94
17	213	-212
18	108	103
19	115	107
20	192	210
21	113	89
22	62	60
23	69	59
24	84	-68
25	0	16
1	2	L
1	2442	-2629
2	366	-362
3	316	336
4	22	5
5	770	-771
6	612	617
7	92	-93
8	410	-415
9	51	-70
10	167	-171
11	415	395
12	248	245
13	108	87
14	118	109
15	374	373
16	96	-78
17	313	313
18	73	81
19	134	-153
20	70	-53
21	158	-161
22	96	-86
23	69	-65
24	78	74
25	69	56
1	3	L
1	1858	-1891
2	1652	1720
3	235	240
4	938	956
5	895	892
6	554	-576
7	703	686
8	497	491
9	373	-375
10	657	653
11	118	-114
12	37	9
13	118	-115
14	157	-154
15	69	-35
16	148	-140
17	76	62
18	217	229
19	65	-63
20	74	69
21	97	-110
22	0	-40
23	108	-99
24	51	-18
1	4	L
1	1115	-1121
2	287	-258
3	79	-88
4	91	-71
5	228	228
6	183	175
7	223	229
8	334	-319
9	82	68
10	345	-326
11	317	309
12	64	40
13	130	-129
14	413	423
15	127	114
16	86	63
17	51	69
18	467	-477
19	108	-115
20	199	-203
21	91	98
22	62	42
23	115	109
24	110	110
1	5	L
1	365	363
2	622	622
3	396	412
4	906	878
5	47	-67
6	93	-99
7	24	-57
8	976	-955
9	102	-80
10	570	-564
11	172	-160
12	92	78
13	64	42
14	89	99
15	127	119
16	167	-157
17	112	-90
18	115	-121
19	90	-82
20	120	-106
21	49	-7
22	20	-26
23	42	24
24	101	96
1	6	L
1	874	863
2	82	-61
3	939	918
4	99	-93
5	699	-674
6	261	274
7	568	-536
8	158	140
9	353	352
10	89	-105
11	413	407
12	188	-175
13	159	-146
14	215	-202
15	322	-323
16	0	26
17	221	-214
18	51	48
19	31	-38
20	88	70
21	169	169
22	12	-13
23	134	124
1	7	L
1	765	769
2	517	516
3	384	378
4	908	-886
5	555	-558
6	617	-630
7	360	-346
8	202	-211
9	36	-17
10	282	291
11	256	250
12	81	-85
13	78	42
14	0	-5
15	79	-70
16	171	181
17	56	68
18	99	-108
19	81	57
20	58	43
21	119	122
22	5	-23
23	69	57
1	8	L
1	354	337
2	158	-170
3	57	57
4	49	38
5	331	334
6	80	86
7	186	169
8	479	469
9	317	-330
10	0	39
11	350	-355
12	205	-216
13	174	-177
14	389	-388
15	112	134
16	61	-67
17	107	115
18	207	220
19	126	-113
20	132	127
21	122	-134
22	72	67
1	9	L
1	246	-239
2	69	-67
3	72	-81
4	152	-155
5	399	-389
6	84	-76
7	66	20
8	190	198
9	267	272
10	226	245
11	59	52
12	111	81
13	217	-216
14	63	-50
15	95	46
16	51	47
17	126	127
18	128	136
19	62	-76
20	61	52
21	0	6
1	10	L
1	281	-282
2	75	-26
3	54	24
4	174	179
5	445	446
6	227	-219
7	100	101
8	147	-150
9	270	-291
10	55	31
11	325	-343
12	236	230
13	130	129
14	71	68
15	158	171
16	32	-48
17	51	22
18	42	-40
19	64	76
20	78	-51
21	62	-74
1	11	L
1	142	-144
2	322	304
3	211	-196
4	167	172
5	180	169
6	97	-70
7	83	92
8	160	169
9	0	-19
10	109	126
11	129	-114
12	48	-32
13	15	-13
14	199	-209
15	79	61
16	73	-77
17	42	-67
18	37	42
19	51	-10
20	21	-17
1	12	L
1	159	171
2	241	239
3	319	-335
4	98	79
5	254	-255
6	217	-219
7	71	44
8	285	-290
9	102	107
10	66	-47
11	184	167
12	236	255
13	179	180
14	269	261
15	92	-66
16	123	104
17	76	-82
18	50	-43
1	13	L
1	119	124
2	175	171
3	78	55
4	91	50
5	53	62
6	158	-141
7	107	104
8	71	-77
9	78	16
10	59	-26
11	0	-23
12	75	-4
13	0	11
14	52	52
15	0	3
16	27	26
17	49	-21
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1	58	13
2	312	-322
3	164	-159
4	109	-91
5	146	-146
6	136	132
7	32	-1
8	96	109
9	112	106
10	81	68
11	92	80
12	66	-57
13	66	66
14	109	-94
15	7	-30
16	70	-46
1	15	L
1	75	94
2	99	-95
3	51	-54
4	84	4
5	114	-112
6	48	-33
7	0	10
8	25	-11
9	96	-9
10	65	-22
11	94	87
12	0	27
13	51	44
14	39	29
1	16	L
1	53	-36
2	94	82
3	63	-11
4	33	-22
5	82	92
6	51	32
7	91	97
8	85	59
9	40	-22
10	62	55
11	150	-160
12	62	-80
1	17	L
1	51	10
2	65	-59
3	108	-95
4	78	-30
5	27	-31
6	50	59
7	0	0
8	88	80
9	60	-35
1	18	L
1	55	6
2	137	147
3	59	72
2	0	L
0	376	-367
2	137	129
4	808	791
6	88	87
8	242	253
10	36	-61
12	306	-303
14	242	239
16	305	312
18	113	104
20	54	-21
22	144	-152
24	40	51
2	1	L
0	1581	-1638
1	614	598
2	349	359
3	138	134
4	337	-334
5	935	941
6	675	675
7	217	224
8	373	-383
9	595	614
10	263	-270
11	53	-3
12	101	93
13	183	-173
14	38	25
15	325	-328
16	281	278
17	87	71
18	90	58
19	375	361
20	238	-254
21	152	167
22	159	-142
23	109	-104
24	66	-89
25	63	-77
2	2	L
0	320	321
1	339	334
2	143	-143
3	405	-419
4	1010	-1007
5	695	-725
6	152	-152
7	454	-453
8	104	89*
9	102	-127
10	407	390
11	34	-13
12	79	64
13	128	127
14	177	-164
15	88	93
16	137	168
17	24	-46
18	70	-72
19	161	-179
20	50	-38
21	35	-13
22	112	92
23	88	83
24	47	0
2	3	L
0	2205	-2303
1	579	-577
2	1116	1144
3	166	-159
4	316	310
5	144	-151
6	136	-134
7	287	-299
8	252	-266
9	558	-568
10	95	78
11	94	97
12	293	-293
13	239	249
14	40	-42
15	69	56
16	433	444
17	327	-338
18	82	72
19	183	-188
20	224	-222
21	101	-99
22	58	-37
23	117	118
24	85	-76
2	4	L
0	262	-261
1	1303	-1348
2	275	267
3	177	174
4	574	-582
5	746	759
6	553	-560
7	63	28
8	73	85
9	355	-358
10	269	285
11	465	-435
12	74	63
13	27	20
14	169	-162
15	190	-198
16	214	-210
17	76	-60
18	51	-76
19	60	-39
20	64	11
21	36	-39
22	87	79
23	43	-31
24	31	26
2	5	L
0	1265	1258
1	143	139
2	455	461
3	152	-144
4	512	-523
5	546	-560
6	430	-414
7	347	-336
8	288	291
9	757	-757
10	231	227
11	126	134
12	50	-13
13	228	221
14	261	-280
15	421	429
16	27	0
17	154	-164
18	50	32
19	207	-223
20	195	200
21	74	-68
22	147	162
23	45	31
24	67	62
2	6	L
0	965	955
1	74	-78
2	308	323
3	427	-430
4	361	358
5	358	-347
6	542	553
7	633	684
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17	96	95
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2	22	40
3	164	-155
4	58	25
5	66	-72
6	48	28
7	71	39
8	34	-12
9	123	111
10	66	38
11	43	6
12	110	112
13	15	0
14	39	17
8	13	L
0	392	393
1	36	-26
2	106	103
3	59	-26
4	147	-137
5	65	55
6	115	-122
7	0	13
8	94	-71
9	58	51
10	55	71
11	40	22
12	89	102
8	14	L
0	196	-194
1	0	14
2	132	-131
3	49	-41
4	38	29
5	117	-104
6	65	63
7	0	20
8	59	-56
9	79	66
10	77	-73
8	15	L
0	38	20
1	118	-122
2	0	38
3	198	-190
4	66	56
5	0	-14
6	57	34
7	140	144
9	0	L
2	84	-80
4	339	330
6	250	262
8	212	-191
10	48	-6
12	204	174
14	128	-116
16	69	-33
18	89	74
20	0	-19
9	1	L
1	200	-206
2	64	30
3	267	256
4	281	275
5	147	155
6	68	-51
7	54	75
8	178	-181
9	93	-88
10	153	-173
11	239	-243
12	306	318
13	156	-160
14	126	128
15	208	205
16	172	-175
17	144	155
18	116	-111
19	141	-148
20	179	-169
21	161	-166
9	2	L
1	70	-44
2	433	-443
3	75	77
4	55	-56
5	187	162
6	240	245
7	33	28
8	124	-119
9	55	62
10	113	-110
11	188	196
12	118	125
13	139	147
14	127	122
15	21	-41
16	51	14
17	145	-137
18	58	-52
19	71	-77
20	72	20
9	3	L
1	419	419
2	355	361
3	93	-93
4	205	200
5	167	-172
6	411	-413
7	140	-162
8	99	-81
9	121	114
10	106	101
11	279	282
12	210	195
13	100	107
14	156	150
15	138	-125
16	18	36
17	200	-210
18	96	-88
19	80	66
20	122	-122
9	4	L
1	379	-369
2	168	-162
3	81	67
4	166	-153
5	69	52
6	87	-61
7	141	-134
8	0	-8
9	150	167
10	72	-65
11	227	241
12	54	-70
13	85	-76
14	111	94
15	0	-33
16	67	48
17	51	3
18	55	30
19	70	-10
20	39	-20
9	5	L
1	129	-110
2	370	-369
3	46	-56
4	330	-324
5	291	-279
6	137	124
7	54	55
8	344	340
9	53	35
10	136	149
11	45	81
12	69	-75
13	99	104
14	154	-146
15	77	-22
16	94	79
17	46	-50
18	224	222
19	50	-43
9	6	L
1	0	14
2	135	-128
3	47	-49
4	155	159
5	128	-111
6	234	236
7	102	-85
8	116	118
9	142	-136
10	165	-210
11	70	-15
12	144	-150
13	61	17
14	47	-15
15	49	6
16	78	-45
17	68	42
18	67	-62
19	0	14
9	7	L
1	303	-306
2	140	-155
3	248	-256
4	13	14
5	266	283
6	77	29
7	228	248
8	75	77
9	235	-229
10	63	2
11	281	-289
12	71	-60
13	78	-3
14	212	-206
15	128	130
16	113	-114
17	143	143
18	60	47
9	8	L
1	160	154
2	239	259
3	160	165
4	4	3
5	123	109
6	93	-75
7	84	-62
8	209	214
9	155	-178
10	128	128
11	131	-141
12	85	-83
13	59	9
14	83	-98
15	0	-3
16	75	-58
17	21	7
9	9	L
1	173	175
2	462	462
3	58	-55
4	241	246
5	117	122
6	194	-197
7	143	138
8	409	-419
9	93	78
10	108	-100
11	211	-232
12	80	85
13	63	-21
14	93	92
15	65	54
16	53	-48
9	10	L
1	42	30
2	64	64
3	71	40
4	64	-68
5	75	65
6	100	-78
7	107	73
8	81	-36
9	37	-18
10	63	33
11	24	-12
12	69	47
13	58	41
14	54	70
15	52	-27
9	11	L
1	308	300
2	50	25
3	61	4
4	49	-21
5	168	-176
6	71	-6
7	106	-88
8	17	-41
9	144	126
10	0	38
11	229	232
12	91	66
13	48	44
14	40	35
9	12	L
1	85	-102
2	91	-67
3	83	-73
4	71	-83
5	0	13
6	109	-87
7	46	10
8	46	-70
9	14	-27
10	40	15
11	56	34
12	52	44
9	13	L
1	63	-51
2	140	-131
3	40	-33
4	0	-54
5	56	-46
6	55	62
7	41	-44
8	206	212
9	64	3
10	122	115
9	14	L
1	35	-20
2	52	-16
3	85	-82
4	42	-28
5	0	-3
6	47	-29
7	48	43
8	14	-9
9	15	L
1	113	-120
2	52	36
3	62	14
10	0	L
0	434	-439
2	323	-340
4	0	-31
6	93	91
8	178	188
10	29	24
12	78	34
14	54	-3
16	178	175
18	79	-66
10	1	L
0	464	484
1	159	170
2	68	-11
3	443	463
4	316	-322
5	119	112
6	185	-193
7	334	-328
8	156	-153
9	285	-280
10	168	165
11	91	76
12	270	274
13	164	151
14	87	109
15	117	-112
16	138	-131
17	35	-19
18	56	-49
19	63	-72
10	2	L
0	377	-398
1	68	85
2	64	-72
3	235	245
4	287	295
5	50	62
6	0	-30
7	53	-70
8	68	-65
9	0	6
10	180	184
11	147	-146
12	59	-5
13	173	166
14	85	-52
15	77	-36
16	25	8
17	116	-110
18	0	19
19	174	-179
10	3	L
0	0	0
1	229	-223
2	98	-103
3	455	-452
4	288	-292
5	229	-220
6	235	-226
7	225	213
8	51	-11
9	402	422
10	179	168
11	131	150
12	144	164
13	152	-145
14	121	95
15	63	-36
16	88	-78
17	77	68
18	0	14
19	169	166
10	4	L
0	401	420
1	223	223
2	248	248
3	246	246
4	168	-171
5	78	-71
6	59	0
7	43	23
8	67	-3
9	109	105
10	47	-54
11	65	-81
12	23	-28
13	71	-70
14	22	-37
15	76	45
16	110	-77
17	53	32
18	58	34
19	51	-21
10	5	L
0	183	-184
1	92	-70
2	255	-237
3	89	-67
4	39	-16
5	100	89
6	329	340
7	135	124
8	161	166
9	76	-71
10	217	-217
11	49	-21
12	301	-304
13	0	18
14	85	-63
15	8	-19
16	201	197
17	0	-3
18	113	126
10	6	L
0	142	147
1	114	-106
2	152	158
3	49	-28
4	60	-65
5	28	11
6	52	-88
7	190	182
8	86	-94
9	45	38
10	127	-150
11	92	-74
12	18	1
13	98	-90
14	50	-48
15	28	0
16	49	2
17	0	21
18	47	33
10	7	L
0	480	476
1	171	173
2	134	143
3	346	355
4	42	24
5	54	56
6	98	72
7	267	-275
8	89	112
9	212	-213
10	123	-124
11	73	-70
12	174	-184
13	62	39
14	50	-5
15	37	14
16	45	12
17	150	-150
10	8	L
0	109	112
1	78	43
2	151	-159
3	0	0
4	0	13
5	135	-122
6	110	108
7	132	-133
8	38	33
9	66	-27
10	175	-162
11	64	68
12	39	-49
13	58	-1
14	121	120
15	26	2
16	40	18
10	9	L
0	448	444
1	118	119
2	172	184
3	0	-27
4	224	-220
5	65	-68
6	199	-202
7	62	-46
8	146	139
9	70	-37
10	209	218
11	0	10
12	92	92
13	89	90
14	68	-73
15	73	55
10	10	L
0	0	81
1	29	0
2	54	-50
3	129	-134
4	64	-81
5	30	-18
6	27	-14
7	151	-147
8	97	91
9	94	-109
10	122	123
11	99	81
12	96	96
13	117	122
14	42	36
10	11	L
0	224	-241
1	143	-142
2	95	-104
3	198	-203

the hydrogen atoms. During the final cycle of refinement all parameter shifts were less than 35% of the estimated standard deviations.

The final R index for all 3932 reflections is 0·091. The R index based on $F^2(=\sum|F_o^2-F_c^2|/\sum F_o^2)$ is 0·085. The final goodness of fit, $\{\sum w(F_o^2-F_c^2/k^2)^2/(m-s)\}^{1/2}$, where m is the number of reflections used and s is the number of parameters refined, is 1·98. Table 2 lists the observed

Table 2 (*cont.*)

4	91	-60
5	65	-7
6	64	-35
7	202	201
8	0	8
9	172	181
10	71	95
11	0	4
12	18	56
10	12	L
0	117	-88
1	69	-82
2	42	-18
3	72	-53
4	0	-44
5	67	53
6	68	-44
7	36	63
8	0	5
9	61	77
10	115	116
11	48	7
10	13	L
0	98	-93
1	60	-66
2	79	-74
3	68	-57
4	20	-25
5	68	66
6	65	75
7	103	105
8	0	16
10	14	L
0	0	-29
1	41	-11
2	0	-18
3	24	34
4	55	17
11	0	L
2	546	570
4	793	825
6	219	224
8	109	-103
10	278	-274
12	116	94
14	136	121
16	104	-86
18	212	-214
11	1	L
1	69	67
2	330	-324
3	166	-151
4	136	-144
5	306	-306
6	54	-53
7	283	-279
8	171	190
9	63	78
10	83	76
11	231	231
12	125	-114
13	58	66
14	59	-26
15	79	-66
16	55	-12
17	57	-39
18	60	59
11	2	L
1	913	936
2	216	-214
3	244	248
4	75	-97
5	191	-197
6	157	160
7	306	-335
8	194	200
9	134	-151
10	62	-20
11	84	93
12	53	-33
13	129	140
14	65	20
15	179	-177
16	50	7
17	229	-239
18	17	-8
11	3	L
1	34	15
2	294	-303
3	69	83
4	394	-393
5	206	198
6	35	10
7	150	143
8	248	242
9	45	-23
10	55	-33
11	212	-219
12	138	-134
13	97	-104
14	44	48
15	90	85
16	0	34
17	117	109
18	22	3
11	4	L
1	150	-169
2	549	-562
3	48	13
4	544	-552
5	221	230
6	70	-37
7	174	170
8	139	133
9	169	-170
10	50	58
11	171	-172
12	119	-125
13	42	-60
14	67	-33
15	52	-14
16	95	106
17	41	59
11	5	L
1	0	46
2	133	123
3	139	126
4	73	59
5	91	105
6	61	-58
7	145	137
8	93	-123
9	23	-5
10	80	-76
11	53	-36
12	19	7
13	99	-94
14	93	105
15	69	-52
16	55	28
17	54	31
11	6	L
1	447	-454
2	60	-39
3	177	-157
4	169	166
5	169	171
6	0	13
7	98	92
8	303	-321
9	73	-18
10	208	-216
11	104	-97
12	68	42
13	88	69
14	42	51
15	106	114
16	55	-14
11	7	L
1	40	18
2	101	82
3	92	-85
4	99	113
5	133	-137
6	100	93
7	62	39
8	72	46
9	91	99
10	77	-41
11	75	76
12	30	-23
13	77	77
14	57	-2
15	88	-74
11	8	L
1	137	146
2	237	239
3	95	-88
4	122	107
5	99	-93
6	0	-32
7	105	-79
8	108	-98
9	87	71
10	56	41
11	130	122
12	79	68
13	135	138
14	92	70
15	12	9
11	9	L
1	127	-134
2	155	-157
3	64	-18
4	85	-96
5	41	38
6	200	187
7	76	-82
8	116	133
9	42	-22
10	69	70
11	91	72
12	46	-27
13	90	67
11	10	L
1	47	-56
2	133	-137
3	174	182
4	68	-50
5	24	-12
6	83	108
7	119	-105
8	138	151
9	31	44
10	133	135
11	143	156
12	64	32
11	11	L
1	108	-104
2	90	-111
3	77	46
4	0	35
5	77	83
6	0	26
7	68	39
8	79	-79
9	68	-84
10	6	-32
11	12	L
1	89	-73
2	35	-9
3	39	0
4	38	6
5	89	67
6	51	43
7	80	67
8	99	108
11	13	L
1	61	58
2	54	35
3	47	18
4	84	67
12	0	L
0	65	9
2	173	173
4	284	284
6	74	-62
8	218	-233
10	119	101
12	245	252
14	81	-73
16	357	-366
12	1	L
0	439	441
1	36	34
2	163	163
3	51	3
4	162	-174
5	219	-225
6	66	0
7	179	-184
8	64	63
9	43	-39
10	53	-53
11	164	-164
12	72	18
13	0	-13
14	140	138
15	0	-11
16	46	-41
17	12	11
12	2	L
0	67	34
1	117	-117
2	68	-65
3	311	-327
4	57	35
5	234	-242
6	152	139
7	82	36
8	69	-32
9	118	118
10	115	-101
11	147	-141
12	16	-42
13	218	-209
14	82	64
15	0	-35
16	56	25
12	3	L
0	129	-88
1	114	104
2	73	18
3	85	-68
4	65	53
5	165	-153
6	144	136
7	111	113
8	44	35
9	167	170
10	0	3
11	130	126
12	38	13
13	74	8
14	41	-2
15	89	92
16	5	5
12	4	L
0	541	-566
1	0	19
2	176	-169
3	43	47
4	268	261
5	44	41
6	105	116
7	177	-176
8	110	-100
9	175	-186
10	158	-151
11	54	36
12	95	-83
13	81	77
14	90	77
15	57	49
16	202	205
12	5	L
0	124	-131
1	0	15
2	178	-182
3	236	259
4	167	-169
5	284	299
6	94	88
7	69	76
8	204	208
9	50	7
10	65	-9
11	112	106
12	76	-36
13	0	-4
14	70	-41
15	0	-44
12	6	L
0	107	89
1	336	346
2	53	7
3	468	483
4	141	-148
5	48	-3
6	83	-62
7	236	-227
8	75	75
9	34	-37
10	90	65
11	150	146
12	76	65
13	172	167
14	64	-31
12	7	L
0	228	235
1	67	38
2	58	25
3	68	60
4	69	-22
5	131	133
6	135	-119
7	40	20
8	88	-64
9	37	-82
10	48	4
11	31	-35
12	38	18
13	79	-58
14	59	55
12	8	L
0	160	162
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4	47	-57
5	85	94
6	244	-245
7	122	144
8	58	-34
9	77	91
10	253	263
11	25	17
12	151	157
13	40	-30
12	9	L
0	49	51
1	142	-113
2	96	93
3	215	-222
4	0	54
5	102	-81
6	0	-7
7	98	-109
8	72	-49
9	47	-24
10	60	-45
11	36	34
12	10	L
0	101	-118
1	53	-80
2	44	17
3	187	-187
4	93	89
5	100	-79
6	62	96
7	103	111
8	0	-19
9	127	120
10	80	-88
12	11	L
0	104	-103
1	72	-53
2	38	4
3	50	-4
4	0	-28
5	47	-8
6	37	-37
7	64	-37
12	12	L
0	60	-17
1	47	-24
2	56	-41
3	15	-9
4	0	3
13	0	L
2	106	-93
4	135	-126
6	57	0
8	252	240
10	23	-38
12	231	-243
14	162	-166
13	1	L
1	123	125
2	102	92
3	128	-119
4	31	-2
5	90	-78
6	124	114
7	85	82
8	186	182
9	93	79
10	68	86
11	71	46
12	80	-63
13	0	30
14	39	-3
15	99	-92
13	2	L
1	66	54
2	63	-65
3	156	155
4	31	-52
5	208	221
6	0	8
7	96	95
8	51	-28
9	181	-177
10	59	-4
11	284	-279
12	0	-1
13	57	-72
14	55	70
15	182	183
13	3	L
1	66	58
2	247	-250
3	70	-62
4	149	139
5	76	-74
6	354	366
7	0	-16
8	77	85
9	74	53
10	42	28
11	17	-5
12	41	4
13	62	-43
14	65	-5
13	4	L
1	65	-59
2	350	351
3	8	19
4	131	135
5	118	-117
6	135	-137
7	54	12
8	184	-187
9	78	-4
10	27	31
11	76	73
12	179	186
13	0	-27
14	153	145
13	5	L
1	90	-64
2	83	-57
3	75	69
4	27	-17
5	60	53
6	45	-9
7	9	-7
8	60	-60
9	71	-58
10	0	-28
11	105	-86
12	15	3
13	25	-13
13	6	L
1	57	58
2	99	-99
3	114	-110
4	81	79
5	203	-208
6	138	144
7	134	-127
8	39	55
9	133	133
10	44	-28
11	228	232
12	41	-18
13	7	L
1	11	40
2	115	-99
3	60	29
4	59	-50
5	58	-48
6	50	-50
7	96	-85
8	132	-129
9	58	30
10	113	-112
11	75	49
13	8	L
1	71	-46
2	218	-227
3	100	95
4	165	-193
5	139	159
6	22	47
7	3	-4
8	150	144
9	67	-57
10	91	91
13	9	L
1	111	-99
2	103	-66
3	99	102
4	89	-95
5	0	8
6	35	39
7	97	-88
8	99	102
13	10	L
1	105	-94
2	14	19
3	70	57
4	61	56
5	124	119
6	78	-50
13	11	L
1	43	-54
14	0	L
0	81	-51
2	76	55
4	215	225
6	299	304
8	0	0
10	213	-221
12	118	-137
14	1	L
0	99	-100
1	110	-106
2	51	-48
3	153	-149
4	103	110
5	63	19
6	146	121
7	133	133
8	53	4
9	111	108
10	94	-83
11	48	-48
12	104	-118
14	2	L
0	100	-65
1	130	130
2	46	6
3	258	262
4	61	13
5	142	138
6	37	-28
7	104	-119
8	57	-44
9	146	-150
10	39	-2
11	87	71
12	68	58
14	3	L
0	177	-197
1	157	152
2	0	-27
3	180	185
4	95	55
5	37	-9
6	95	-40
7	136	-142
8	76	6
9	101	-83
10	76	-81
11	46	53
12	42	-34
14	4	L
0	52	-15
1	70	-29
2	74	-54
3	0	-12
4	136	-118
5	35	26
6	224	-219
7	52	31
8	57	-62
9	74	62
10	152	144
11	109	110
14	5	L
0	37	60
1	52	73
2	10	61
3	144	127
4	109	-117
5	66	5
6	231	-222
7	60	-66
8	79	-59
9	78	-74
10	132	121
14	6	L
0	34	-11
1	141	-118
2	0	-22
3	139	-153
4	97	88
5	9	-32
6	93	95
7	25	-14
8	35	25
9	44	53
14	7	L
0	87	76
1	97	-96
2	77	49
3	219	-223
4	86	77
5	134	-123
6	0	5
7	132	128
8	70	-89
14	8	L
0	121	-126
1	93	106
2	55	40
3	75	73
4	139	154
5	102	-95
6	70	81
14	9	L
0	163	-162
1	31	-10
2	46	-27
3	64	-61
15	0	L
2	101	-92
4	112	110
6	87	93
8	54	-3
15	1	L
1	38	-41
2	187	189
3	0	-20
4	129	131
5	91	73
6	33	-31
7	128	120
8	146	-147
9	80	-68
15	2	L
1	68	-48
2	43	19
3	0	11
4	53	-28
5	55	-12
6	42	-5
7	15	-24
8	38	18
9	77	72
15	3	L
1	67	59
2	135	120
3	45	-24
4	62	92
5	197	-203
6	30	-18
7	123	-124
8	105	-101
9	83	85
15	4	L
1	76	-72
2	21	-22
3	39	9
4	63	-10
5	58	22
6	83	-66
7	40	50
8	88	-78
15	5	L
1	139	131
2	239	-247
3	76	-55
4	100	-122
5	0	-11
6	59	51
7	27	25
15	6	L
1	34	-11
2	89	91
3	63	59
4	53	-38
5	45	28
15	7	L
1	91	-104
2	80	-73
16	0	L
0	27	-42
2	48	37
4	119	118
16	1	L
0	157	131
1	79	73
2	67	58
3	169	172
4	102	-78
16	2	L
0	54	-29
1	113	108
2	43	-2
3	71	82
4	51	-38
16	3	L
0	125	122
1	101	-99
2	27	39

Table 3. *Final parameters for the nonhydrogen atoms and their standard deviations*

All values have been multiplied by 10^5. The temperature factors are of the form $\exp\,[-(h^2\beta_{11}+\ldots+kl\beta_{23})]$.

	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
P	16786 (4)	13614 (4)	9242 (3)	347 (3)	−38 (6)	−5 (4)	370 (2)	9 (4)	168 (1)
N(1)	20792 (15)	22131 (13)	13004 (10)	580 (12)	−95 (21)	−96 (14)	477 (10)	−85 (13)	224 (5)
N(2)	14904 (14)	6828 (14)	15001 (9)	460 (11)	58 (20)	102 (13)	516 (10)	115 (13)	212 (5)
C(1)	24989 (17)	9838 (16)	3841 (10)	400 (12)	−48 (22)	25 (16)	418 (11)	47 (13)	193 (5)
C(2)	22618 (18)	9722 (17)	−2391 (10)	496 (14)	−67 (24)	76 (15)	467 (12)	4 (14)	192 (5)
C(3)	13953 (17)	11908 (16)	−5082 (11)	504 (14)	−135 (23)	−25 (15)	470 (13)	−25 (14)	181 (5)
C(4)	6486 (17)	14610 (17)	−1319 (11)	449 (13)	−102 (24)	−128 (15)	471 (12)	58 (16)	224 (6)
C(5)	6523 (16)	15813 (16)	5010 (11)	375 (12)	−16 (21)	−9 (15)	460 (12)	26 (14)	189 (5)
C(6)	22266 (26)	29684 (20)	9102 (15)	1064 (25)	−443 (34)	54 (29)	534 (15)	−67 (23)	432 (10)
C(6′)	28008 (24)	21721 (22)	17962 (15)	900 (22)	113 (38)	−518 (23)	832 (19)	−417 (22)	404 (8)
C(7)	9975 (24)	9514 (23)	20769 (14)	1020 (23)	404 (40)	443 (22)	910 (20)	300 (22)	288 (7)
C(7′)	12262 (23)	−1776 (19)	13206 (15)	874 (22)	−316 (32)	101 (26)	525 (15)	220 (21)	431 (9)
C(8)	35150 (16)	8523 (16)	5799 (11)	377 (12)	14 (21)	68 (14)	409 (11)	15 (14)	214 (5)
C(9)	37603 (18)	3941 (18)	11036 (12)	454 (14)	−85 (26)	11 (18)	609 (15)	251 (18)	291 (7)
C(10)	47036 (20)	3100 (21)	12854 (14)	500 (16)	54 (31)	−129 (21)	815 (18)	426 (22)	408 (9)
C(11)	54175 (20)	6563 (23)	9399 (16)	437 (15)	−9 (32)	−93 (24)	871 (20)	313 (27)	506 (10)
C(12)	51939 (21)	11125 (24)	4234 (16)	453 (16)	−202 (34)	204 (22)	1041 (23)	393 (26)	454 (10)
C(13)	42487 (19)	12186 (20)	2430 (13)	443 (14)	−43 (29)	107 (18)	748 (17)	280 (19)	305 (7)
C(14)	12643 (18)	11761 (16)	−11872 (11)	574 (15)	−304 (23)	−21 (16)	468 (12)	−37 (14)	187 (5)
C(15)	17352 (23)	5857 (19)	−15567 (12)	944 (21)	−68 (35)	−96 (21)	592 (15)	−39 (18)	220 (6)
C(16)	16247 (26)	5939 (22)	−21992 (13)	1214 (27)	−194 (42)	38 (25)	763 (19)	−151 (20)	230 (7)
C(17)	10552 (25)	11828 (20)	−24732 (13)	1237 (27)	−550 (40)	−148 (23)	826 (18)	47 (21)	187 (6)
C(18)	5797 (22)	17757 (20)	−21194 (12)	819 (19)	−448 (32)	−183 (20)	724 (17)	204 (19)	241 (7)
C(19)	6911 (19)	17670 (18)	−14843 (11)	610 (15)	−305 (27)	−70 (17)	582 (14)	27 (17)	206 (6)
C(20)	−2457 (17)	18286 (19)	8211 (11)	419 (13)	254 (26)	4 (16)	662 (14)	274 (16)	228 (6)
C(21)	−10918 (20)	14185 (22)	6613 (15)	440 (15)	53 (32)	87 (21)	806 (19)	338 (23)	438 (9)
C(22)	−19535 (22)	16733 (26)	9402 (18)	484 (17)	55 (37)	105 (26)	1221 (25)	764 (30)	621 (12)
C(23)	−19494 (24)	23009 (28)	13824 (16)	811 (20)	1153 (41)	393 (25)	1559 (29)	700 (29)	439 (10)
C(24)	−11266 (24)	27078 (27)	15397 (15)	968 (22)	1404 (40)	136 (25)	1515 (29)	−2 (28)	324 (10)
C(25)	−2842 (21)	24695 (23)	12590 (13)	678 (17)	711 (33)	24 (21)	1010 (20)	−122 (23)	276 (8)

and calculated structure factors. The final heavy atom parameters and their standard deviations are given in Table 3; those for the hydrogen atoms are given in Table 4. Since the block-diagonal approximation was used for the least-squares refinement, the e.s.d.'s in Tables 3 and 4 are probably underestimates of the true values and perhaps should be increased. With the calculated standard deviations increased by 50%, the average estimated standard deviations in the positional parameters are about 0·001, 0·003, 0·005, and 0·04 Å for the P, N, C, and H atoms.

Table 4. *Final parameters of the hydrogen atoms*

The *x*, *y*, *z* values have been multiplied by 10^4.

	x	*y*	*z*	*B*
H(2)	2766 (14)	844 (13)	−523 (9)	3·8 (5)
H(4)	78 (14)	1603 (12)	−333 (8)	3·2 (5)
H(9)	3273 (17)	145 (14)	1355 (10)	5·5 (6)
H(10)	4829 (19)	−35 (17)	1643 (11)	7·2 (7)
H(11)	6105 (21)	630 (20)	1072 (13)	9·6 (9)
H(12)	5629 (20)	1324 (18)	167 (13)	8·6 (8)
H(13)	4058 (20)	1544 (18)	−127 (12)	7·9 (8)
H(15)	2093 (18)	168 (15)	−1376 (10)	6·6 (7)
H(16)	2009 (19)	197 (16)	−2418 (12)	7·9 (7)
H(17)	958 (18)	1216 (16)	−2902 (12)	6·8 (7)
H(18)	164 (17)	2223 (15)	−2294 (11)	6·8 (7)
H(19)	361 (16)	2170 (14)	−1249 (9)	4·6 (5)
H(21)	−1082 (18)	931 (17)	354 (11)	6·7 (7)
H(22)	−2479 (21)	1334 (18)	784 (13)	9·1 (8)
H(23)	−2519 (24)	2384 (22)	1617 (14)	11·9 (10)
H(24)	−1110 (22)	3236 (22)	1834 (15)	11·3 (10)
H(25)	332 (21)	2741 (19)	1379 (13)	9·3 (9)
H(61)	1758 (22)	2962 (20)	581 (14)	10·6 (9)
H(62)	2913 (21)	2949 (19)	736 (13)	9·1 (8)
H(63)	2160 (26)	3463 (22)	1195 (15)	12·7 (10)
H(64)	3457 (27)	2164 (26)	1636 (17)	15·4 (12)
H(65)	2687 (24)	2650 (20)	2073 (19)	11·7 (10)
H(66)	2660 (21)	1587 (18)	2049 (13)	9·0 (8)
H(71)	1231 (22)	1560 (21)	2189 (15)	11·3 (10)
H(72)	355 (23)	804 (22)	2034 (15)	11·4 (10)
H(73)	1190 (20)	538 (19)	2410 (14)	10·2 (9)
H(74)	616 (21)	−199 (18)	1219 (12)	9·2 (8)
H(75)	1447 (17)	−305 (16)	891 (11)	6·8 (7)
H(76)	1334 (20)	−575 (19)	1670 (12)	9·0 (8)

At the conclusion of refinement, a three-dimensional electron density difference map was calculated with only the heavy atom contributions included in the values for the calculated structure factors. This map showed regions of electron density in excess of 0·35 e.Å^{-3} at all hydrogen positions. A final difference Fourier synthesis calculated with both heavy atom and hydrogen atom contributions included in the values for the calculated structure factors showed no peaks or troughs exceeding 0·35 e.Å^{-3} in magnitude.

Description and discussion of the structure

Fig. 2 shows a stereoscopic view of the molecule. Bond distances and angles involving only heavy atoms are listed in Table 5. The C–H bond lengths range from 0·91 to 1·09 Å. The twelve N–C–H angles of the methyl groups have a mean value of 108°.

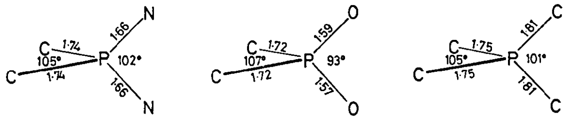
Table 5. *Bond distances and bond angles*

These values contain no corrections for thermal motions. Standard deviations were calculated from the values of Table 3, increased by 50%.

P——N(1)	1·660 (3) Å	C(9)—C(10)	1·383 (6) Å
P——N(2)	1·658 (3)	C(10)–C(11)	1·360 (7)
P——C(1)	1·741 (4)	C(11)–C(12)	1·362 (7)
P——C(5)	1·737 (4)	C(12)–C(13)	1·389 (6)
N(1)–C(6)	1·467 (6)	C(14)–C(15)	1·388 (6)
N(1)–C(6′)	1·474 (6)	C(14)–C(19)	1·383 (6)
N(2)–C(7)	1·486 (5)	C(15)–C(16)	1·398 (6)
N(2)–C(7′)	1·450 (6)	C(16)–C(17)	1·355 (7)
C(1)–C(2)	1·388 (5)	C(17)–C(18)	1·375 (7)
C(1)–C(8)	1·498 (5)	C(18)–C(19)	1·382 (6)
C(2)–C(3)	1·388 (5)	C(20)–C(21)	1·391 (6)
C(3)–C(4)	1·390 (5)	C(20)–C(25)	1·381 (6)
C(3)–C(14)	1·480 (5)	C(21)–C(22)	1·406 (7)
C(4)–C(5)	1·381 (5)	C(22)–C(23)	1·371 (8)
C(5)–C(20)	1·486 (5)	C(23)–C(24)	1·359 (8)
C(8)–C(9)	1·384 (5)	C(24)–C(25)	1·377 (7)
C(8)–C(13)	1·383 (5)		

N(1)–P——N(2)	101·6 (2)°	C(1)—C(8)—C(9)	122·5 (3)°
N(1)–P——C(1)	112·3 (2)	C(1)—C(8)—C(13)	119·9 (4)
N(1)–P——C(5)	112·2 (2)	C(9)—C(8)—C(13)	117·5 (4)
N(2)–P——C(1)	113·0 (2)	C(8)—C(9)—C(10)	121·2 (4)
N(2)–P——C(5)	113·0 (2)	C(9)—C(10)–C(11)	120·4 (5)
C(1)–P——C(5)	105·0 (2)	C(10)–C(11)–C(12)	119·4 (4)
P——N(1)–C(6)	114·4 (3)	C(11)–C(12)–C(13)	120·8 (5)
P——N(1)–C(6′)	123·6 (3)	C(12)–C(13)–C(8)	120·6 (4)
C(6)–N(1)–C(6′)	110·9 (4)	C(3)—C(14)–C(15)	121·5 (4)
P——N(2)–C(7)	121·5 (3)	C(3)—C(14)–C(19)	121·5 (4)
P——N(2)–C(7′)	115·8 (3)	C(15)–C(14)–C(19)	117·0 (4)
C(7)–N(2)–C(7′)	111·7 (4)	C(14)–C(15)–C(16)	120·9 (5)
P——C(1)–C(2)	119·9 (3)	C(15)–C(16)–C(17)	120·4 (5)
P——C(1)–C(8)	118·9 (3)	C(16)–C(17)–C(18)	120·0 (4)
C(2)–C(1)–C(8)	120·0 (3)	C(17)–C(18)–C(19)	119·5 (5)
C(1)–C(2)–C(3)	127·8 (4)	C(18)–C(19)–C(14)	122·3 (4)
C(2)–C(3)–C(4)	119·1 (4)	C(5)—C(20)–C(21)	118·9 (4)
C(2)–C(3)–C(14)	121·4 (4)	C(5)—C(20)–C(25)	122·8 (4)
C(4)–C(3)–C(14)	119·5 (4)	C(21)–C(20)–C(25)	118·2 (4)
C(3)–C(4)–C(5)	128·2 (4)	C(20)–C(21)–C(22)	119·5 (5)
P——C(5)–C(4)	119·9 (3)	C(21)–C(22)–C(23)	119·9 (5)
P——C(5)–C(20)	120·3 (3)	C(22)–C(23)–C(24)	120·9 (5)
C(4)–C(5)–C(20)	119·6 (3)	C(23)–C(24)–C(25)	119·2 (6)
		C(24)–C(25)–C(20)	122·2 (5)

The four ligands around the phosphorus atom form a distorted tetrahedron, with approximate *mm*2 symmetry. The dihedral angle between the planes C(1), P, C(5) and N(1), P, N(2) is 89·9°. The angles C(1)–P–C(5) and N(1)–P–N(2) are smaller than a perfect tetrahedral angle of 109·5°; the other bond angles involving P are larger than 109·5°. Similar geometry around the phosphorus atom was found in the related



(*a*) (*b*) (*c*)

Fig. 3. Comparison of the coordination of the phosphorus atom in (*a*) present compound, (*b*) 1,1-dimethoxy-2,4,6-triphenylphosphorin (Thewalt, 1969), (*c*) 1,1-dimethyl-2,4,6-triphenylphosphorin (Daly, 1970).

compounds 1,1-dimethyl-2,4,6-triphenylphosphorin (Daly & Märkl, 1969; Daly, 1970) and 1,1-dimethoxy-2,4,6-triphenylphosphorin (Thewalt, 1969). Fig. 3 compares the bonding to P in the three compounds. Although the stereochemistry is approximately the same for these three phosphorins, it appears that the π-bonding in systems (*a*) and (*b*) of Fig. 3 is different from that in system (*c*). The O and N atoms in (*a*) and (*b*) have a lone pair of electrons which might participate in π-bonding with appropriate $3d$ orbitals of P [Cruickshank's (1961) concept of d_π-p_π bonding]. In 1,1-dimethyl-2,4,6-triphenylphosphorin [Fig. 3(*c*)] no such additional π-bonding is possible.

Evidence for the double bond character of the P–N bonds is provided by their lengths (1·660 and 1·658 Å); these bonds are considerably shorter than single bonds (1·77 Å in [PO_3–NH_3]Na; Cruickshank, 1964). The possibility of P–N π-bonding is also consistent with the finding that the amino groups are more nearly planar than nonconjugated amino groups [the sum of the bond angles at N(1) equals 348·9° and at N(2) equals 349·0°, compared with the 328·5° expected for an undistorted, tetrahedral amino group]. π-bonding between P and N also has been proposed to explain the relatively short exocyclic P–N bonds in tetrameric and hexameric phosphonitrilic dimethylamides (Wagner & Vos, 1968; Bullen, 1962).

The two P–C bond distances of 1·741 and 1·737 Å are equal within experimental error and are intermediate between the lengths expected for P–C single bonds and those expected for P–C double bonds involving tetracoordinate phosphorus [1·823 and 1·661 Å in $(C_6H_5)_3P{=}CH_2$; Bart, 1969]. Similar P–C distances (between 1·72 and 1·75 Å) were found in the phosphorins depicted in Fig. 3(*b*) and (*c*) as well as in phosphorins with no exocyclic substituents bonded to the phosphorus atom (Fischer, Hellner, Chatzidakis & Dimroth, 1968; Bart & Daly, 1968). Phosphorus bonding which is similar to that found in the phosphorins occurs in the phosphamethin cations (III) and (IV).

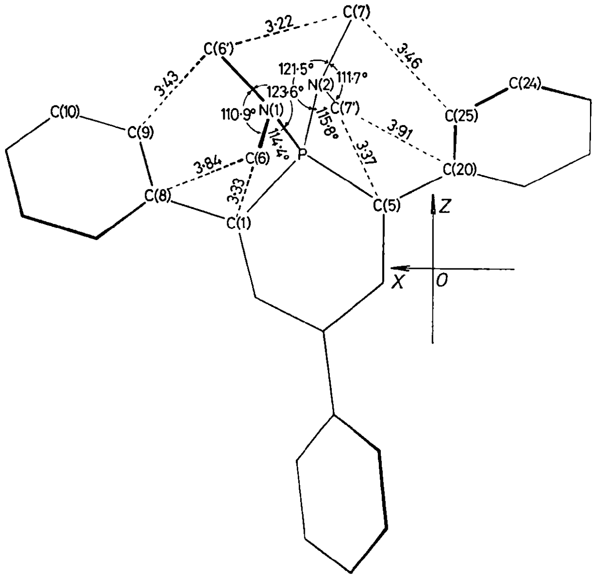
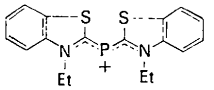
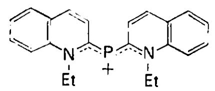


Fig. 4. A view of a molecule along the *y* axis showing selected bond angles and non-bonded intramolecular contacts. For complete labeling of atoms, see Fig. 1.



(III)



(IV)

The P–C distances in (III) and (IV) range from 1·75 to 1·81 Å and the C–P–C angles are 104·6° (III) and 100·4° (IV) (Allmann, 1966; Kawada & Allmann, 1968). The agreement between the C–P–C angles in cations (III) and (IV) and in the phosphorins gives an indication that the phosphorins are essentially strain-free at P.

The PC_5 central ring is almost planar. Table 6 lists the deviations of atoms from the least-squares plane through the ring (plane I). To compensate for the relatively small C–P–C angle (105·0°) the average of the other ring angles must be greater than 120°. Actually, only two angles [at C(2) and C(4)] are larger than 120°. The remaining ring angles are nearly equal to 120°. Similar distributions of ring angles were found in 1,1-dimethoxy-2,4,6-triphenylphosphorin and in 1,1-dimethyl-2,4,6-triphenylphosphorin. The four C–C bond lengths of the PC_5 ring do not deviate significantly from their average value of 1·387 Å, and are in close agreement with the C–C bond distances present in other aromatic systems.

The geometry of the PC_5 ring indicates a delocalized 6π-electron system, similar to that found in benzene or pyridine. It is likely that the π-bonding in the PC_5 ring accounts for the relatively high stability of the compound. There has been much discussion about possible models for π-bonding in phosphorus compounds (Craig, MacColl, Nyholm, Orgel & Sutton, 1954; Cruickshank, 1961; Mitchell, 1969; Coulson, 1969; Marsmann, Van Wazer & Robert, 1970; Bartell, Su & Yow, 1970).

The $3p_z$, $3d_{xz}$, and $3d_{yz}$ orbitals of phosphorus all have suitable symmetry for conjugation with the $2p_z$ orbitals of the aromatic carbon atoms (z perpendicular to the PC_5 plane; x in the P–C(3) direction; y completing an orthogonal set of axes). Recent molecular orbital calculations by Oehling & Schweig (1970) using the CNDO method (Complete Neglect of Differential Overlap) have shown that the $3p_z$ orbital of phosphorus makes a large contribution to the π-bonding in 1,1-dimethoxy-2,4,6-triphenylphosphorin. The calculations also demonstrate that the phosphorus d orbitals make a major contribution to the P–C σ bonds. It is reasonable to expect that similar results would be obtained from molecular orbital calculations for 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin.

The lengths of the eighteen C–C bonds in the phenyl rings range from 1·355 to 1·406 Å. The mean value is 1·379 Å, which is somewhat shorter than the value of 1·394 Å expected for C–C aromatic bonds (Sutton, 1965). This apparent bond shortening may be due to the omission of thermal-vibration corrections. Information concerning least-squares planes through the phenyl groups is given in Table 6 (planes II, III and IV). The phenyl groups intersect the central ring with dihedral angles ranging from 32·5 to 47·4°. Comparable dihedral angles of *ca.* 45° have been observed in gaseous triphenylbenzene (Bastiansen, 1949).

Table 6. *Deviations from, and angles between the least-squares planes*

The equations of the planes (with x, y, z representing fractional coordinates) are in the form: Deviation (Å) =

(Plane I)	$4{\cdot}461x+14{\cdot}714y-2{\cdot}663z-2{\cdot}492$
(Plane II)	$-0.908x+13{\cdot}068y+11{\cdot}826z-1{\cdot}485$
(Plane III)	$-2{\cdot}138x+10.610y-15{\cdot}555z-0{\cdot}718$
(Plane IV)	$10{\cdot}896x+9{\cdot}744y-1{\cdot}735z-2{\cdot}731$

Plane		Deviation	Plane		Deviation
I	P	0·014 Å	III	C(20)	−0·002
	C(1)	−0·032		C(21)	−0·008
	C(2)	0·011		C(22)	0·013
	C(3)	0·018		C(23)	−0·010
	C(4)	−0·018		C(24)	0·001
	C(5)	−0·008		C(25)	0·005
	C(8)*	0·176			
	C(11)*	0·640	IV	C(14)	−0·001
	C(14)*	0·119		C(15)	0·001
	C(17)*	0·378		C(16)	0·000
	C(20)*	−0·130		C(17)	0·001
	C(23)*	−0·344		C(18)	−0·001
	N(1)*	1·346		C(19)	0·001
	N(2)*	−1·222			
II	C(8)	−0·005			
	C(9)	−0·007			
	C(10)	0·013			
	C(11)	−0·008			
	C(12)	−0·002			
	C(13)	0·009			

Planes	Angle between planes
I, II	45·9°
I, III	47·4
I, IV	32·5

Atoms excluded from the calculations of the least-squares planes are indicated by an asterisk.
P was given twice the weight of a C atom.

The N–P–N angle of 101·6° is slightly larger than the O–P–O angle in 1,1-dimethoxy-2,4,6-triphenylphosphorin; this is probably due to steric repulsion between the dimethylamino groups. The closest intramolecular, nonbonded contact between methyl carbon atoms is C(6′)–C(7) = 3·22 Å. The average N–C distance is 1·469 Å; the average P–N–C and C–N–C angles are 118·8° and 111·3°, respectively. The P–N–C bond angles cover a fairly large range of values; similar disparities among P–N–C angles have been found in other molecules containing $P[N(CH_3)_2]_2$ groups (Bullen, 1962; Wagner & Vos, 1968; Born, 1969). The conformations of the methylamino groups and the twist of phenyl rings II and III are such that the molecule has approximate C_2 symmetry, with the pseudo twofold axis passing through atoms C(3) and P. As a consequence of this, corresponding intramolecular nonbonded contacts of the two sets of dimethylamino groups with their neighboring phenyl rings are very similar. This geometry is depicted in Fig. 4. The crystal packing is shown in Fig. 5. There are no unusually short intermolecular contacts. Ellipsoids depicting the thermal motion of the nonhydrogen atoms are shown in Fig. 2. The thermal motion is consistent with the molecular geometry; the central ring and its immediate substituents are vibrating in a nearly isotropic pattern, while the phenyl and methyl groups show considerable anisotropic motion.

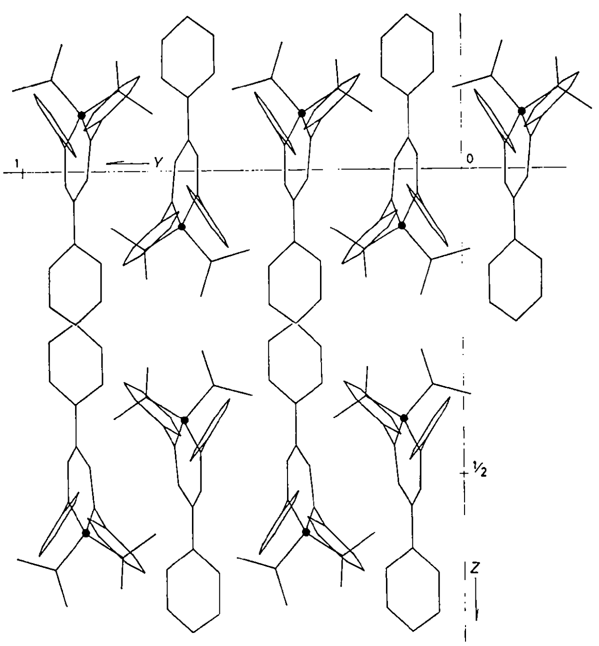


Fig. 5. Projection of the structure along the x axis.

The computer programs used in this study included the thermal ellipsoid plotting program *ORTEP* (Johnson, 1965); the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962); and a block-diagonal least-squares program, which was obtained from Dr James Trotter at the University of British Columbia. The other programs were written in our laboratories.

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The Crystal and Molecular Structure of Pyreno-(1′, 2′ : 1, 2)-pyrene. An Example of the Use of Linear Least-Squares for Structure Solution

BY KENNETH W. MUIR AND J. MONTEATH ROBERTSON
Chemistry Department, The University, Glasgow W2, Scotland

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Pyreno-(1′,2′:1,2)-pyrene, $C_{30}H_{16}$, crystallizes in the monoclinic system. There are four molecules in a cell of dimensions $a=13\cdot17$, $b=7\cdot71$, $c=20\cdot32$ Å, $\beta=118\cdot5°$. The space group is $P2_1/c$. The structure was solved in the *b*-axis projection by molecular transform techniques. The *y* coordinates were subsequently derived by a linear least-squares procedure. The structure has been refined by block-diagonal least-squares methods to a conventional *R* value of 0·11 over 2284 intensity data, measured on a linear diffractometer. As a result of intramolecular overcrowding the molecule is propeller shaped, the minimum non-bonding C···C and H···H distances involving overcrowded atoms being 2·96 and 2·03 Å respectively. The observed bond lengths are in agreement with those predicted by simple VB and MO arguments.

In hydrocarbons of the 3,4-benzphenanthrene type a planar carbon skeleton would result in a non-bonded hydrogen–hydrogen contact of approximately 0·5 Å. Ferguson & Robertson (1963) and Trotter (1964) have reviewed the structural studies of such molecules. From these studies it is clear that the intramolecular overcrowding is mainly relieved by out of plane distortions spread over the entire carbon skeleton of the molecule; no study, however, is sufficiently accurate for any conclusions to be made regarding the effect of the overcrowding on bond distances and angles.

On the basis of a comparison between the observed bond lengths and those calculated from various theoretical models, Burns & Iball (1960) have suggested that in chrysene, overcrowding is at least partly relieved by extension of two of the carbon–carbon bonds by 0·03–0·04 Å; this suggestion has been widely accepted (*e.g.* Cruickshank & Sparks, 1960; Coulson & Haigh, 1963). The overcrowded hydrogen atoms in chrysene are about 1·7 Å apart. Since 3,4-benzphenanthrene and its derivatives are much more severely overcrowded than chrysene, larger departures of the bond lengths from predicted values might be expected. To investigate this we have determined the structure of pyrenopyrene.

Experimental

Crystal data

Pyrenopyrene, $C_{30}H_{16}$, F.W. 376·5. Monoclinic, $a=13\cdot17$, $b=7\cdot71$, $c=20\cdot32$ Å; $\beta=118\cdot5°$; $V=1813$ Å^3;