hydrogen bonding interaction. Table 5 shows that the phenylalanyl ring has large thermal parameters while the tyrosine ring does not. The tyrosine is not fixed by hydrogen bonding, so the reason for the difference must be the packing of the groups around the rings. The motion of the phenylalanine ring is relatively unrestricted in the direction of the thermal ellipsoids. On the other hand, the tyrosine ring is held in place by its own symmetry-related partner, the phenylalanine ring and the carboxyl group.

In most of the molecules containing peptide-type linkages that have been studied in the solid state by X-ray crystallography, the atoms surrounding the peptide bonds have been found to be coplanar. The nonplanar peptides which have been found to this date have been in small cyclic compounds or in peptides containing proline (Winkler & Dunitz, 1971; Ramachandran, 1968). Although the peptide group in this molecule is in a *trans* configuration, the dihedral angle about the peptide bond is 17·7° [$\omega = 162·3$ (4)°]. Table 7 shows the results of fitting a least-squares plane to the atoms comprising the peptide group. In this molecule, the twist in the peptide plane must be caused by the crystal-packing forces. The molecule is not forced into its configuration by internal bonding as in cyclic compounds. It seems likely that if such forces can produce a nonplanar peptide in a small polypeptide, the various interactions in a protein structure could also produce nonplanar peptides.

Table 7. *Deviations from the least-squares plane through* C(3), C(4), O(2), N(2), C(5)

C(3)	0·090Å
C(4)	−0·062
O(2)	−0·007
N(2)	−0·129
C(5)	0·108

As in all crystallographic studies that are undertaken to study the chemistry of the molecules, questions must be raised concerning the structures of the molecules when not in the crystal. Because of the crystal-packing forces, it is possible that the structure of the molecule in the crystal is not the same as that in biological systems or in solution. This could obviate any chances of explaining the kinetics of the pepsin catalyzed hydrolysis on the basis of the solid-state results. Nevertheless, the structure found is useful for comparative purposes and as a point of departure for other methods. Other techniques such as n.m.r. spectroscopy or energy minimization programs would be useful in determining the structure of the molecule in solution.

We wish to thank the members of the local X-ray crystallographic community for many helpful discussions.

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The Crystal and Molecular Structure of *cis*-1,3-Diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane

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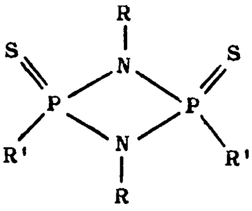
Crystals of the title compound, [NEtP(S)Ph]$_2$, are monoclinic, $a = 7·17$, $b = 16·27$, $c = 16·59$ Å, $\beta = 96·0°$, space group $C2/c$, $Z = 4$. The atomic positions have been determined by least-squares refinement from X-ray diffractometer intensities, the final R being 0·075 for 1574 reflexions. The molecules possess exact symmetry C_2. The phosphazane ring is non-planar with the bond angles N–P–N 84·5° and P–N–P 95·0°, the departure from planarity being attributed to steric overcrowding in the molecule. The bond lengths: P–N 1·695, P–S 1·922, P–C 1·797, and N–C 1·46 Å, are not significantly different from the corresponding lengths in the *trans* isomer.

Introduction

The possibility of *cis–trans* isomerism in the cyclodiphosphazanes (I) was first suggested by Trippett (1962) but until recently pairs of isomers had not been separated. Flint, Ibrahim, Shaw, Smith & Thakur (1971) were able to isolate two isomers of 1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane (I: R = Et, R′ = Ph) and to assign *cis* and *trans* configurations to them on the basis of spectral data. We have studied the crystal structures of both these isomers. The structure of the *trans* isomer (melting point 144 °C) was described in an earlier paper (Bullen, Rutherford & Tucker, 1973) and we now present the results on the *cis* isomer (m.p. 137 °C) for comparison. A crystallographic analysis of 1,3-dimethyl-2,4-dichloro-2,4-dithiocyclodiphosphazane (I: R = Me, R′ = Cl) failed to establish whether its configuration was *cis* or *trans*, because the chlorine and sulphur atoms could not be distinguished (Weiss & Hartmann, 1966). With this possible exception, no information has been available on the detailed molecular geometry of *cis*-cyclodiphosphazanes.



(I)

Experimental

Crystals of *cis*-[NEtP(S)Ph]$_2$ are monoclinic six-sided plates on {001} bounded by the forms {110} and {010}. Their unit-cell dimensions were measured from precession photographs and are given in Table 1 with other data.

Table 1. *Crystal data*

cis-[NEtP(S)Ph]$_2$, m.p. 137 °C*	$V = 1925$ Å^3
Monoclinic	$Z = 4$
$a = 7.17\ (\pm 0.02)$ Å	$D_m = 1.26$ g cm^{-3} (by flotation)
$b = 16.27\ (\pm 0.03)$	$D_c = 1.26$ g cm^{-3}
$c = 16.59\ (\pm 0.03)$	$F(000) = 768$
$\beta = 96.0\ (\pm 0.02)°$	λ(Mo $K\alpha$) = 0·7107 Å
Space group $C2/c$ (No. 15)	μ(Mo $K\alpha$) = 4·1 cm^{-1}

Systematic absences: hkl when $h+k$ is odd, and $h0l$ when l is odd.

* Our measurement. Flint *et al.* (1971) report 134 °C.

X-ray intensities comprising the 11 layers of reflexions 0–10, k, l were measured at 22–25 °C on a Philips PAILRED diffractometer with monochromated Mo $K\alpha$ radiation. 1589 reflexions with $I > 2\sigma(I)$ were obtained by measuring all reflexions with sin θ/λ less than 0·7 Å^{-1} and some in the range 0·7–0·8 Å^{-1}. The crystal used was approximately 0·4 × 0·3 × 0·1 mm in size. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The least-squares refinement was carried out initially at the Atlas Computer Laboratory, Chilton, with the X-RAY 63 program package, and in the final stages on the University of Essex PDP-10 computer with a program written by G. M. Sheldrick. The atomic scattering factors were calculated by the analytic function $f = C + \sum_{i=1}^{4} A_i \exp(-B_i \sin^2\theta/\lambda^2)$, the parameters A, B, and C being taken from Cromer & Waber (1965) for sulphur, phosphorus, nitrogen, and carbon, and from Forsyth & Wells (1959) for hydrogen.

Structure determination

The systematic absences indicate space group Cc or $C2/c$. The positions of the phosphorus and sulphur atoms were deduced from the Patterson function, in which the distribution of peaks corresponded to the centrosymmetric space group $C2/c$. This choice of space group was confirmed by the subsequent analysis and refinement.

The carbon and nitrogen atoms were located from Fourier syntheses phased on the heavier atoms. Five cycles of full-matrix least-squares refinement with isotropic temperature factors reduced R to 0·16. Hydrogen atoms were then inserted, the positions of those in the phenyl and methylene groups being calculated from the molecular geometry with a C–H bond length of 1·05 Å. Those in the methyl group were located from a difference synthesis and their positions adjusted to make the C–H distances equal to 1·05 Å.

Least-squares refinement was continued with anisotropic temperature factors for all atoms except hydrogen. In the later cycles the weighting scheme $w = (9.5 - 0.4|F_o| + 0.0065|F_o|^2)^{-1}$ was used to make the average $w\Delta^2$ (where $\Delta = |F_o| - |F_c|$) similar in size over

Table 2. *Fractional atomic coordinates with estimated standard deviations*

	x/a	y/b	z/c
S	0·17825 (23)	0·31134 (9)	0·13677 (9)
P	0·09576 (17)	0·21641 (8)	0·19159 (7)
N	0·1333 (5)	0·2094 (3)	0·2935 (2)
C(1)	0·1704 (7)	0·1215 (3)	0·1508 (3)
C(2)	0·1854 (8)	0·1148 (3)	0·0674 (3)
C(3)	0·2411 (10)	0·0415 (4)	0·0360 (4)
C(4)	0·2915 (11)	−0·0242 (4)	0·0855 (4)
C(5)	0·2768 (13)	−0·0181 (4)	0·1677 (4)
C(6)	0·2163 (11)	0·0546 (4)	0·1995 (3)
C(7)	0·2980 (9)	0·2334 (5)	0·3470 (3)
C(8)	0·3381 (11)	0·1790 (6)	0·4158 (5)

Table 3. *Components of thermal vibration tensors* (Å^2, × 10^3) *and their estimated standard deviations*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	68·5 (10)	49·2 (8)	47·8 (8)	13·3 (6)	23·1 (7)	3·2 (7)
P	41·3 (6)	41·3 (7)	26·1 (5)	3·2 (5)	9·2 (4)	5·4 (6)
N	40 (2)	57 (3)	29 (2)	4 (2)	5 (1)	−1 (2)
C(1)	51 (3)	45 (3)	34 (2)	3 (2)	13 (2)	8 (2)
C(2)	67 (4)	56 (3)	37 (3)	2 (2)	21 (2)	9 (3)
C(3)	91 (5)	68 (4)	51 (3)	−10 (3)	22 (3)	6 (4)
C(4)	103 (6)	61 (4)	67 (4)	−12 (3)	20 (4)	21 (4)
C(5)	128 (7)	62 (4)	57 (4)	6 (3)	6 (4)	30 (4)
C(6)	111 (6)	55 (4)	43 (3)	2 (3)	15 (3)	18 (4)
C(7)	54 (3)	99 (5)	41 (3)	6 (3)	−6 (2)	−14 (3)
C(8)	73 (5)	149 (8)	69 (5)	30 (5)	−25 (4)	−4 (5)

Table 4. *Fractional coordinates and mean-square amplitudes of thermal vibration assigned to hydrogen atoms (numbered according to the carbon atom to which they are attached)*

	x/a	y/b	z/c	$\overline{u^2}$ (Å^2)
H(2)	0·154	0·165	0·029	0·08
H(3)	0·246	0·036	−0·027	0·08
H(4)	0·340	−0·079	0·061	0·08
H(5)	0·312	−0·068	0·206	0·08
H(6)	0·206	0·059	0·262	0·08
H(7*a*)	0·414	0·237	0·314	0·08
H(7*b*)	0·279	0·294	0·368	0·08
H(8*a*)	0·448	0·196	0·457	0·10
H(8*b*)	0·359	0·120	0·395	0·10
H(8*c*)	0·217	0·172	0·446	0·10

the whole range of $|F_o|$ and $\sin\theta/\lambda$. 15 weak reflexions for which $4|F_c|<|F_o|$ were excluded from the refinement. Neither the positions nor the temperature factors of hydrogen atoms were refined. The final R is 0·075 for 1574 reflexions and R' $[=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}]$ is 0·085. For the total set of 1589 reflexions $R=0·078$. In the last cycle all parameter changes were less than 0·12σ. An attempt to refine the structure in the space group *Cc* gave no improvement.

The final atomic coordinates and thermal parameters with estimated standard deviations are listed in Tables 2–4. The molecular shape and the numbering of the atoms are shown in Fig. 1. Observed and calculated structure factors are given in Table 5. Bond lengths and bond angles are listed in Table 6. The orientation and magnitudes of the principal axes of the vibration ellipsoids are given in Table 7. The anisotropic thermal parameters were analysed in terms of a rigid-body motion for the central part of the mol-

Table 5. *Observed and calculated structure factors* (×10)

L	$\lvert F_o\rvert$	F_c
0, 22, L		
6	123	41
1	143	153
0, 20, L		
12	118	-56
5	126	119
1	215	-230
0	105	-83
0, 18, L		
15	100	-29
11	123	70
10	155	143
8	249	-245
7	119	125
4	142	153
2	143	-121
1	228	206
0, 16, L		
14	202	184
10	313	-303
8	339	336
4	266	-256
3	156	163
2	112	116
0, 14, L		
17	100	-87
16	119	150
15	106	60
14	167	-159
12	99	-80
10	412	404
9	104	-185
8	334	-344
7	122	139
6	110	126
5	203	195
4	278	256
2	359	-357
0, 12, L		
20	108	-53
19	137	-149
18	166	147
17	159	177
16	133	-152
13	146	-127
12	199	202
11	139	131
10	253	-231
8	303	323
7	152	155
6	186	-185
5	481	-492
4	82	-24
2	270	273
1	673	699
0	709	-758
0, 10, L		
22	102	45
21	147	-68
19	202	109
17	217	-225
16	217	214
14	128	144
13	288	284
12	123	-132
11	111	-92
7	400	-409
6	159	156
5	398	425
4	404	-390
3	84	71
2	281	-281
1	724	-768
0	642	680
0, 8, L		
19	109	-147
18	185	207
17	195	202
16	114	-114
14	120	-95
12	411	411
10	94	-110
9	624	-621
8	243	-252
7	483	503
6	143	-129
5	297	-322
4	97	121
3	297	-293
2	232	213
1	923	903
0	608	-633
0, 6, L		
20	103	-77
19	197	206
17	127	-115
16	113	-76
15	286	278
14	109	110
13	131	-134
11	684	-677
10	294	-266
9	939	907
8	481	387
7	902	-874
6	81	-80
5	609	-566
4	601	-586
3	1254	1235
2	332	356
1	367	-406
0	373	378
0, 4, L		
21	141	100
18	164	-178
16	122	124
15	129	-128
14	200	-203
13	378	386
12	163	-173
11	133	127
10	491	466
9	1256	-1290
8	530	-493
7	490	437
6	590	575
5	512	491
4	133	109
3	491	-509
2	799	-849
1	316	335
0	1209	1291
0, 2, L		
23	107	43
21	123	-136
20	104	-141
19	107	68
18	325	342
16	325	-319
14	216	-234
13	125	-85
12	391	392
11	105	-83
10	251	-233
9	793	757
8	91	30
7	727	-665
6	757	-693
5	813	-726
4	857	786
2	1289	1250
1	992	-1015
0	1335	-1451
0, 0, L		
24	133	-96
20	185	197
18	524	-530
16	250	212
14	328	356
12	371	-353
10	93	91
8	1045	-907
6	1083	987
4	1540	-1420
2	1186	-1102
1, 21, L		
6	147	-123
2	249	237
0	161	-151
-1, 21, L		
2	135	-83
4	130	95
1, 19, L		
9	109	107
8	107	-126
2	210	-216
0	163	183
-1, 19, L		
4	138	-124
5	122	82
7	183	-163
1, 17, L		
15	107	-90
11	232	244
10	111	-85
9	229	-246
8	122	124
6	131	-116
5	219	218
2	146	125
0	94	-89
-1, 17, L		
3	186	-178
5	143	-131
7	368	360
9	146	-132
11	136	-89
13	135	120
1, 15, L		
17	129	-141
15	109	133
13	101	90
11	308	-330
9	234	221
5	146	-166
4	91	103
2	103	69
1	109	101
-1, 15, L		
1	387	-395
2	142	-148
3	322	325
7	382	-359
9	366	343
10	103	-74
13	266	-228
14	102	67
1, 13, L		
19	120	-122
15	101	-85
14	112	137
11	358	375
9	305	-323
6	205	221
5	111	107
4	105	120
3	351	-365
2	208	-205
1	453	452
0	147	137
-1, 13, L		
1	141	138
4	276	-285
5	163	-189
6	114	-120
7	371	359
9	231	-211
10	228	216
12	99	-105
13	134	119
14	156	-152
15	157	-121
16	164	178
1, 11, L		
20	160	-175
19	112	153
17	137	-153
15	100	-65
14	168	-174
13	109	111
9	227	246
8	239	255
7	305	-341
6	193	-211
5	197	225
4	79	-73
3	162	162
2	741	781
1	602	-650
0	508	-533
-1, 11, L		
1	259	-270
2	268	-295
3	113	-111
4	307	311
6	164	-178
9	95	98
10	270	-240
11	257	-247
12	133	132
14	118	137
15	183	200
16	322	-310
17	117	-96
18	175	167
20	141	91
1, 9, L		
20	168	169
18	204	-243
17	154	100
14	90	50
10	441	456
8	387	-411
7	419	450
6	310	307
5	404	-415
3	608	-642
2	714	-758
1	574	608
0	616	632
-1, 9, L		
2	80	73
3	538	516
4	99	-111
7	363	-541
8	267	-245
11	244	222
12	208	-195
13	181	-172
15	203	-194
16	246	253
18	111	-92
1, 7, L		
20	152	-187
18	175	196
16	180	-193
15	104	-114
13	203	215
12	486	511
11	325	348
10	607	-609
9	251	-281
8	311	341
7	512	-524
6	254	247
4	381	-395
3	209	227
2	152	152
1	257	-261
0	504	-532
-1, 7, L		
1	82	-91
2	969	984
3	179	-228
4	145	-129
5	438	411
6	737	-703
7	674	666
8	860	782
9	126	-77
10	395	-383
11	542	-515
12	333	-315
14	306	316
16	143	-141
17	163	-130
18	130	129
21	135	133
1, 5, L		
20	138	135
19	113	132
18	165	-161
16	357	395
14	205	-209
13	351	364
12	681	-714
11	431	-444
10	893	926
9	227	225
8	370	-373
7	332	344
6	302	-312
5	601	-600
4	675	699
3	292	-315
2	155	158
-1, 5, L		
1	517	-491
2	1421	-1433
3	852	804
4	599	543
5	338	318
6	832	785
7	714	-682
8	886	-813
9	679	630
10	193	188
12	477	467
13	543	-534
14	211	-197
15	145	139
16	108	-109
1, 3, L		
19	266	-290
18	129	127
17	305	319
16	245	-262
15	111	-104
13	282	-281
12	243	232
11	578	574
10	569	-565
9	197	-177
8	450	427
7	408	381
6	120	127
5	403	-378
4	373	-375
3	670	-650
2	973	-961
1	75	77
0	283	-318
-1, 3, L		
1	957	975
2	1879	1957
3	351	-318
4	525	-431
6	568	-530
7	117	116
8	776	726
9	595	-569
10	129	-73
11	226	218
12	273	-233
13	164	152
14	152	162
15	302	-285
17	136	112
19	100	51
20	123	-145
1, 1, L		
21	179	-190
19	396	387
17	293	-312
15	173	-184
13	478	464
12	170	-180
11	166	-160
10	443	406
9	497	433
8	327	-309
7	1080	-960
6	611	-542
5	291	264
4	298	280
3	1191	1065
2	1308	-1212
-1, 1, L		
2	829	756
3	292	-266
4	336	275
5	628	574
6	981	901
8	165	-156
9	201	204
10	293	-271
11	651	-607
12	110	84
15	540	549
17	338	-355
21	163	154
-2, 22, L		
2	101	43
2, 20, L		
4	127	-107
3	206	194
1	106	-93
-2, 20, L		
1	119	123
2, 18, L		
10	108	100
8	121	82
6	118	-136
0	95	93
-2, 18, L		
4	168	-178
6	210	217
10	126	-131
2, 16, L		
15	113	57
12	263	254
10	99	-121
8	95	-87
6	132	139
0	202	-217
-2, 16, L		
1	170	-168
2	211	202
4	247	241
6	408	-397
10	198	177
12	186	-173
2, 14, L		
14	109	119
12	243	-255
7	137	-155
6	116	-116
3	179	193
1	149	-166
0	319	321
-2, 14, L		
1	86	65
3	145	-140
4	284	-279
5	149	-139
6	331	300
8	145	-159
9	244	243
10	193	-188
12	305	260
13	122	-137
14	116	-79
2, 12, L		
14	97	-93
12	92	82
10	166	-198
9	113	-110
8	119	129
7	172	165
2, 12, L		
5	365	389
4	191	-217
3	457	-503
2	378	415
1	106	-102
-2, 12, L		
1	392	-403
2	113	-147
3	292	294
4	214	198
5	91	98
6	178	-186
7	148	-147
9	233	-226
11	133	128
12	169	-181
13	210	216
14	230	195
15	283	-283
19	151	132
2, 10, L		
18	128	-132
11	146	-151
10	138	140
9	459	496
8	279	-297
7	153	-164
6	201	217
5	296	-302
4	301	293
3	669	721
2	339	-370
1	371	-400
-2, 10, L		
1	347	402
2	261	282
3	391	-420
4	215	216
6	133	-134
7	97	77
8	104	-84
9	175	184
10	200	191
11	126	-120
13	250	-241
14	319	-323
15	310	321
17	109	-105
18	105	116
19	137	-125
21	126	166
2, 8, L		
19	131	-150
13	159	-189
12	191	-189
11	421	432
10	120	118
9	291	-298
8	237	249
7	82	74
6	200	-227
5	411	440
3	438	-462
2	221	253
1	114	129
0	190	213
-2, 8, L		
2	351	-376
3	150	172
5	218	-247
6	366	364
7	237	233
8	135	140
9	158	207
10	147	-144
12	296	-267
13	165	167
14	165	191
15	304	-316
16	113	-63
18	226	-218
21	189	-196
2, 6, L		
21	117	-104
19	106	123
17	164	-191
13	334	356
12	154	132
11	417	-423
10	145	-162
9	205	182
8	117	-102
7	441	433
6	263	284
5	83	-96
4	65	64
3	266	-268
2	102	-99
1	326	-336
0	323	-359
-2, 6, L		
1	629	-635
3	325	-325
4	501	496
5	998	983
6	446	-468
7	406	-398
9	106	-106
10	339	332
11	804	792
12	206	-203
13	314	-289
17	116	-126
21	162	179
2, 4, L		
20	144	132
19	174	-172
18	127	-119
17	244	240
15	198	-168
14	254	248
13	376	-378
12	336	-331
11	715	736
10	143	124
8	105	-114
7	171	-177
6	291	-293
4	540	546
3	202	210
2	82	86
1	305	306
0	214	-214
-2, 4, L		
1	779	841
2	188	-195
3	342	-324
4	389	-400
5	589	-589
6	102	122
7	720	696
8	131	-112
9	501	472
11	407	-384
12	338	333
14	212	-200
16	127	135
17	102	93
20	114	-126
21	142	-132
23	154	170
2, 2, L		
20	202	-214
18	115	144
15	91	76
12	130	130
11	416	-412
10	576	-542
9	161	127
8	813	765
7	510	508
6	216	-192
5	379	333
4	981	-940
3	133	110
2	1243	1229
1	454	-466
0	529	-571
-2, 2, L		
1	454	473
2	1245	-1244
3	95	83
4	187	-144
5	662	616
6	292	263
7	322	-303
8	436	442
9	503	-481
10	176	-198
11	328	332
12	185	-187
14	540	533
16	255	-219
20	242	265
22	127	-123
23	164	-201
2, 0, L		
20	211	227
16	106	-85
10	675	612
8	568	-488
6	85	61
4	1469	1294
0	2429	-2463
-2, 0, L		
2	1677	1599
4	297	264
6	498	-470
8	420	360
10	412	424
14	703	-731
16	490	514
18	242	245
20	284	-315
22	212	246
3, 21, L		
5	120	54
4	173	-141
0	142	116
3, 19, L		
5	98	-65
4	115	121
3	111	52
0	174	-148
-3, 19, L		
5	123	102
10	117	-63
12	158	123
3, 17, L		
13	136	-104
12	103	47
9	124	132
7	98	-105
6	124	105
1	107	108
-3, 17, L		
3	274	277
5	243	-254
9	178	175
11	133	-121
12	114	-96
3, 15, L		
15	142	-117
13	183	191
9	110	-113
7	119	113
4	109	-107
1	253	-257
-3, 15, L		
3	354	-381
5	369	376
8	108	91
9	311	-311
11	230	226
3, 13, L		
9	89	78
7	128	-96
6	179	-175
4	158	179
-3, 13, L		
2	143	147
3	254	284
4	125	129
5	201	-202
6	130	118
8	219	-231
9	185	171
11	290	-258
12	255	241
13	162	181
17	112	-53
3, 11, L		
11	200	-195
10	125	-150
6	262	265
5	290	-322
4	424	-451
3	375	398
1	242	264
0	462	503
-3, 11, L		
1	412	439
2	182	-189
7	122	-110
8	149	146
10	105	84
11	237	234
12	314	-305
13	299	-303
14	299	271
15	108	96
18	225	-224
19	114	-104
3, 9, L		
12	223	-214
10	86	103
9	215	-237
6	300	-318
5	387	386
4	429	458
2	156	-163
1	275	-286
0	327	-360
-3, 9, L		
1	209	-223
2	278	319
3	150	-152
4	225	-244
5	172	175
6	331	305
7	192	183
9	259	-246
11	200	-191
12	396	396
13	454	443
14	402	-397
17	200	-190
19	135	99
20	211	-216
3, 7, L		
14	200	-219
13	160	-186
12	154	159
9	273	288
8	213	-233
5	189	-201
2	155	167
1	392	406
-3, 7, L		
1	191	211
2	590	-613
3	85	121
4	702	757
5	562	-589
6	207	-209
7	141	-176
8	406	-398
9	313	320
10	685	670
11	291	288
12	265	-244
17	170	189
18	149	-133
19	110	-106
20	196	224
21	156	-137
22	150	-175
3, 5, L		
18	103	-124
15	119	-141
14	388	399
10	227	-265
9	241	-254
8	261	255
6	101	-104
5	314	292
4	367	-363
3	234	257
2	74	-78
1	139	-139
0	720	769
-3, 5, L		
1	96	103
2	506	522
3	668	-671
4	1313	-1302
5	340	337
6	264	253
9	551	-546
10	717	-692
11	469	471
12	286	286
13	160	175
16	189	167
20	213	-233
22	208	233
3, 3, L		
21	139	163
18	139	114
15	204	221
14	162	-195
13	175	-163
12	234	237
11	100	-109
9	140	-109
8	265	-248
7	86	-91
6	132	155
5	529	529
4	118	104
3	66	-78
2	465	455
1	335	353
0	155	-175
-3, 3, L		
1	288	-318
2	616	-651
3	622	634
4	857	869
5	426	-391
6	363	-342
7	280	291
8	737	-704
9	162	159
10	435	420
11	582	-579
13	464	462
16	145	-133
19	180	173
20	180	217
22	162	-218
3, 1, L		
21	122	-116
17	109	121
15	98	-102
13	90	-78
12	91	49
11	158	-150
9	330	303
8	178	174
7	245	241
6	133	108
5	742	-734
4	199	-178

Table 5 (*cont.*)

L	$\lvert F_o\rvert$	F_c
3	496	478
2	455	402
1	823	752
-3, 1, L		
1	906	956
2	258	-252
3	428	-412
4	559	-520
6	304	-291
8	249	246
11	604	579
13	767	-796
14	86	-82
15	163	172
17	309	330
19	248	-276
21	162	177
22	127	162
-4, 22, L		
1	114	-61
4, 20, L		
7	145	118
1	142	125
-4, 18, L		
2	137	135
3	127	88
4	113	-97
8	153	129
9	109	106
11	135	-132
4, 16, L		
10	130	118
2	132	120
0	129	95
-4, 16, L		
2	397	-398
3	131	-98
4	267	231
5	91	48
6	120	103
8	208	-208
10	150	140
4, 14, L		
16	131	-108
14	166	107
7	149	133
6	145	-140
5	95	-94
4	127	117
3	87	-66
2	146	-127
1	153	148
0	221	-214
-4, 14, L		
2	422	398
3	103	104
4	248	-254
8	263	256
10	195	-196
11	127	136
18	110	92
4, 12, L		
8	153	-175
7	284	-282
6	224	232
5	111	122
4	116	-144
3	166	175
2	213	-220
0	187	202
-4, 12, L		
2	230	-234
4	171	154
7	285	273
9	112	112
10	223	213
11	372	-363
12	259	-232
-4, 12, L		
14	122	80
15	145	147
17	153	-148
4, 10, L		
18	100	78
13	147	164
11	130	-95
9	233	-258
8	135	168
7	423	440
6	339	-341
5	325	-348
4	175	179
3	223	-211
2	196	198
1	497	544
0	353	-382
-4, 10, L		
1	138	158
4	179	-189
5	141	138
6	218	226
7	139	-118
9	112	-116
10	285	-284
11	428	402
12	397	390
13	353	-347
17	227	232
19	143	-131
4, 8, L		
15	139	152
13	116	-128
10	88	-109
9	269	275
7	423	-440
6	185	189
5	182	195
2	243	-244
1	172	-200
0	102	97
-4, 8, L		
1	454	-480
2	149	161
3	480	483
4	165	-154
5	283	-268
6	274	-275
7	131	-129
9	204	187
10	252	240
11	504	-467
12	96	-93
13	382	363
16	179	169
17	140	-131
19	227	253
20	135	-145
21	112	-134
4, 6, L		
17	99	105
16	130	113
15	245	-236
14	116	-113
13	132	121
11	196	180
10	135	142
9	352	-360
8	143	-123
7	121	125
5	133	-142
3	153	189
2	65	84
1	73	44
-4, 6, L		
1	659	679
2	218	-243
3	776	-803
4	158	179
5	110	93
6	198	207
7	347	347
8	240	-242
9	628	-591
10	120	-101
13	100	-76
15	220	243
16	101	-73
17	124	126
19	193	-224
20	113	142
21	141	175
4, 4, L		
17	100	-106
16	179	-172
15	237	238
14	93	83
13	154	-147
11	301	-289
9	344	342
8	270	263
7	177	-168
6	220	-233
3	324	-334
0	99	-74
-4, 4, L		
1	773	-833
2	652	685
3	914	938
4	261	-263
5	363	-349
6	154	145
7	554	-524
8	169	159
9	414	376
10	607	-590
11	187	-158
12	201	193
13	202	188
15	276	-267
18	135	143
19	288	320
21	157	-217
4, 2, L		
18	103	-95
14	235	-226
13	184	173
12	172	163
11	128	103
10	209	188
9	304	-305
8	588	-572
7	121	-103
6	784	728
5	172	-167
4	157	-170
3	158	172
2	723	-669
1	334	325
0	879	910
-4, 2, L		
1	165	176
3	387	-371
4	403	379
5	82	63
6	530	-497
7	407	386
8	184	-167
9	94	-95
10	631	591
11	102	-108
12	725	-705
13	188	-170
14	155	156
15	144	149
16	229	212
18	227	-249
19	162	-180
21	178	176
4, 0, L		
14	140	95
12	334	-305
10	86	-122
8	591	567
6	766	-687
4	265	272
2	1140	1014
0	582	-512
-4, 0, L		
4	161	-157
6	570	565
8	212	-225
10	751	-731
12	897	901
14	188	-164
16	469	-464
18	109	240
5, 19, L		
1	102	51
5, 17, L		
5	111	93
1	129	-125
-5, 17, L		
1	249	-229
5	142	110
6	106	-38
7	138	-141
8	121	-80
10	115	95
5, 15, L		
13	124	-53
7	101	83
5	114	-97
1	148	183
-5, 15, L		
1	331	321
3	155	-162
5	136	-120
7	197	200
5, 13, L		
9	110	120
8	127	139
7	179	-162
5	165	149
4	104	-73
2	147	131
1	156	-163
-5, 13, L		
1	260	-275
3	154	156
4	114	-91
7	123	-113
8	187	182
9	197	172
10	165	-167
11	114	-80
13	103	28
17	106	-67
5, 11, L		
17	136	55
15	131	-76
14	113	-70
10	117	126
9	187	-184
8	188	-202
7	186	226
6	147	157
5	93	-94
4	147	140
3	229	-234
2	179	-188
1	134	143
-5, 11, L		
3	192	-196
4	124	113
5	157	137
6	158	-142
8	177	-179
9	193	-189
10	265	295
11	237	240
14	145	-153
15	115	-128
5, 9, L		
11	93	58
10	201	-218
9	159	164
8	289	298
7	229	-229
6	221	-240
2	354	363
1	80	-72
0	234	-276
-5, 9, L		
2	195	195
3	119	125
4	192	-202
5	294	-301
8	204	204
9	333	329
10	349	-345
11	198	-204
12	212	203
13	132	-156
14	106	104
16	160	-173
5, 7, L		
16	169	162
11	106	-73
10	157	166
8	209	-214
7	111	106
6	261	270
5	129	133
4	191	-197
3	127	-116
1	216	-240
0	476	504
-5, 7, L		
1	170	-186
2	485	-515
4	88	89
5	317	334
6	221	210
7	141	-174
8	230	-226
9	228	-222
12	165	-156
14	140	107
15	139	-117
17	104	-87
18	161	-175
19	164	182
5, 5, L		
18	132	137
16	198	-183
12	128	114
10	106	-106
8	194	195
7	123	106
6	204	-215
5	276	-280
4	347	347
2	90	-95
1	170	180
0	802	-835
-3, 5, L		
1	364	386
2	699	753
4	115	115
5	131	-127
6	360	-333
7	217	223
8	312	301
11	128	-150
13	122	-136
14	249	-249
18	272	255
20	112	-120
5, 3, L		
19	123	103
16	183	155
12	140	-128
10	122	142
9	256	250
8	169	-170
7	424	-411
6	146	144
5	113	130
4	184	-172
2	93	-80
1	460	-482
0	427	442
-5, 3, L		
1	460	-509
2	494	-510
3	219	238
6	437	428
7	248	-245
9	464	478
11	210	-204
12	221	-231
14	176	173
18	218	-266
5, 1, L		
19	118	-98
17	107	111
13	130	129
10	87	-67
9	466	-448
7	652	624
6	116	-100
5	170	-164
4	123	128
3	430	-401
1	386	348
0	147	-153
-5, 1, L		
1	143	197
3	313	-305
4	96	102
5	324	302
9	527	-517
11	503	523
12	91	73
15	257	-290
6, 18, L		
2	114	73
-6, 18, L		
6	104	-49
10	105	-56
6, 16, L		
2	143	-144
0	197	193
-6, 16, L		
4	147	-131
6	140	103
6, 14, L		
10	99	-67
8	119	102
5	148	86
2	164	150
0	174	-181
-6, 14, L		
4	121	98
7	116	117
16	177	-118
6, 12, L		
11	109	-77
10	125	108
9	112	125
8	163	-131
5	120	-107
0	117	91
-6, 12, L		
3	108	108
7	243	-239
8	133	-129
9	218	192
10	116	92
11	101	73
14	106	-97
6, 10, L		
11	149	151
9	192	-152
8	141	135
5	165	159
4	100	-112
1	80	-56
0	106	83
-6, 10, L		
1	112	91
3	123	-137
4	95	-92
7	214	180
8	145	139
9	294	-278
11	95	65
12	118	-124
13	276	233
14	134	104
15	136	-166
6, 8, L		
17	129	-95
11	153	-157
9	171	176
8	127	-110
3	94	133
1	213	-220
-6, 8, L		
1	131	-152
4	203	220
5	128	149
7	149	-173
8	190	-187
9	193	195
13	121	-133
15	166	164
16	148	-100
17	157	-139
6, 6, L		
17	138	122
7	192	176
5	135	-160
4	70	-42
2	66	-66
1	362	369
0	181	197
-6, 6, L		
1	310	326
3	85	97
4	170	-175
5	175	-176
6	76	71
7	146	148
12	105	-81
15	193	-182
17	168	170
18	113	-112
6, 4, L		
13	96	87
11	94	-93
10	97	-114
8	117	107
7	91	-118
5	217	223
3	115	114
2	134	141
1	567	-388
-	257	-294
-6, 4, L		
1	179	-190
3	116	-120
5	305	297
6	207	-198
8	251	249
10	90	91
15	167	161
17	259	-265
18	111	31
21	116	124
6 2, L		
18	144	-91
16	124	113
15	132	-74
12	151	-133
11	148	110
10	235	219
8	167	-165
7	144	128
6	75	-29
5	122	-113
4	154	137
3	122	-111
2	76	-73
1	91	98
-6, 2, L		
1	106	127
2	261	-303
4	144	157
5	154	-116
6	266	243
8	425	-410
10	194	212
11	185	197
12	271	250
14	257	-263
15	133	-111
17	132	140
21	130	-148
6, 0, L		
16	136	-151
14	172	139
12	222	194
10	369	-319
8	226	197
4	303	-261
-6, 0, L		
2	242	296
4	396	-389
6	217	-197
8	556	541
10	248	-251
12	221	-231
14	361	368
7, 15, L		
3	113	-124
-7, 15, L		
3	144	138
7, 13, L		
5	94	-57
3	135	99
-7, 13, L		
5	98	115
7, 11, L		
6	95	-96
-7, 11, L		
2	85	-40
6	103	205
7	113	122
12	166	132
13	150	131
14	105	-62
7, 9, L		
12	107	94
4	139	-145
1	76	26
-7, 9, L		
3	81	49
4	167	151
5	146	126
6	130	-139
7	142	-147
8	123	119
11	133	153
12	190	-190
14	160	156
7, 7, L		
10	119	79
4	145	144
3	145	149
2	196	-234
-7, 7, L		
1	99	75
2	171	185
3	84	-108
4	179	-190
6	99	121
7	133	148
9	116	-68
11	109	-192
14	201	-198
16	172	162
7, 5, L		
11	101	29
8	97	86
5	82	93
4	115	-124
3	149	-158
2	264	298
1	117	129
-7, 5, L		
1	98	-98
2	273	-302
3	120	127
4	202	197
14	253	232
15	133	-115
16	209	-217
7, 3, L		
11	107	-98
9	122	110
5	123	-115
4	111	75
3	152	154
2	171	-163
1	61	-54
-7, 3, L		
2	188	204
3	112	-123
4	178	-192
5	160	183
6	86	-85
7	173	-173
10	93	90
11	156	163
12	94	72
14	178	-183
15	103	132
16	180	186
17	98	-34
7, 1, L		
12	90	36
11	202	176
9	150	-128
7	142	-122
5	214	205
4	68	-56
3	61	-41
-7, 1, L		
2	31	-55
5	254	-240
7	328	321
9	82	-89
10	97	-93
11	295	-288
13	268	283
14	108	87
8, 16, L		
0	105	-60
-8, 16, L		
2	125	78
8, 14, L		
2	99	50
8, 12, L		
7	93	50
-8, 12, L		
2	91	55
4	132	-114
5	105	134
6	111	106
9	115	-102
10	119	-71
12	117	110
-8, 10, L		
3	101	127
4	100	113
5	203	-173
6	115	-96
10	112	99
11	178	-179
8, 8, L		
7	113	63
5	94	-108
3	84	82
-8, 8, L		
3	177	-191
4	86	-91
5	113	145
11	161	157
13	126	-155
8, 6, L		
5	139	141
3	180	-194
2	72	-56
-8, 6, L		
1	203	-212
2	107	103
3	163	-82
5	124	-129
13	252	220
15	126	-148
8, 4, L		
6	91	61
5	151	-151
4	106	-108
3	141	139
2	82	93
0	65	66
-8, 4, L		
1	126	157
2	134	-136
3	133	-163
4	151	162
5	65	45
6	90	-85
13	226	-218
14	121	109
8, 2, L		
6	79	-86
5	116	96
4	38	93
2	74	-60
-8, 2, L		
1	56	-63
2	114	149
3	62	98
4	273	-291
6	213	213
7	79	56
9	94	-75
10	233	-240
12	143	136
13	137	146
8, 0, L		
14	121	-103
6	157	137
0	61	-91
-8, 0, L		
4	388	391
6	280	-281
10	259	265
12	221	-245
16	105	-54
-9, 11, L		
3	111	96
9, 9, L		
6	108	73
-9, 9, L		
3	100	-85
5	82	43
9, 7, L		
8	113	80
6	130	-118
0	100	-104
-9, 7, L		
2	79	102
4	73	-88
10	109	-79
11	101	63
12	177	138
9, 5, L		
6	133	119
4	131	-111
0	127	135
-9, 5, L		
3	62	33
6	100	-63
11	98	-73
12	196	-173
14	118	96
9, 3, L		
7	118	93
6	94	-81
0	57	-81
-9, 3, L		
1	75	88
5	91	95
6	93	87
10	82	-83
12	131	123
9, 1, L		
9	119	108
7	95	-107
3	71	-46
-9, 1, L		
1	93	-102
3	150	208
5	138	-160
9	156	158
-10, 8, L		
3	81	-44
10, 6, L		
1	80	-64
10, 2, L		
0	59	-76
-10, 2, L		
2	66	98

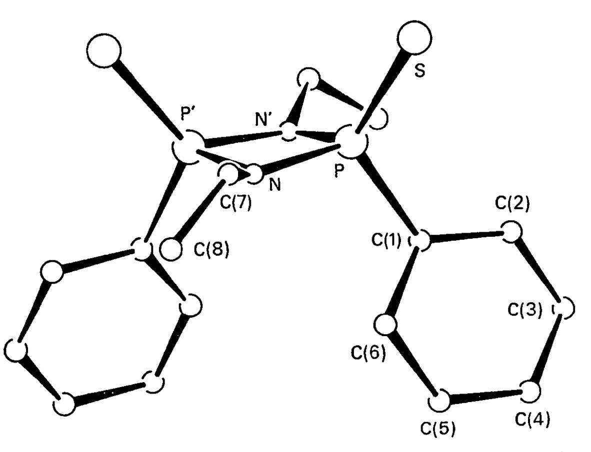


Fig. 1. Molecular shape and numbering of the atoms. A primed atom is related to the corresponding unprimed atom by rotation about the diad axis of the molecule.

ecule comprising the phosphazane ring, sulphur atoms, and carbon atoms C(1), C(1′), C(7), and C(7′). The remaining carbon atoms were not included because it was thought unlikely that the whole molecule behaves as a rigid body. The translational and librational tensors (Table 8) are referred to axes parallel to the inertial axes of this group of 10 atoms but the position of the origin of the librational axes was varied to give the best fit of observed and calculated U_{ij} values (Pawley, 1963). Because of the molecular symmetry, one of the axes of **T** and **ω** (chosen as axis 3) must coincide with the crystallographic diad axis so that $T_{13}=T_{23}=0$ and $\omega_{13}=\omega_{23}=0$. Axis 1 is very nearly parallel to the P···P′ line and axis 2 to the N′···N line. The position obtained for the origin (0, 0·196, 0·250) is displaced from the phosphazane ring by 0·3 Å towards the side occupied by the phenyl groups, *i.e.* towards the centre of gravity of the whole molecule. Since ω_{12} is also zero

(Table 8) the principal axes of ω are parallel to the inertial axes of the group of 10 atoms. This is not the case for the translational tensor. Bond lengths corrected for the effect of the molecular oscillations (Cruickshank, 1956, 1961) are given in Table 6(*b*). The correction is particularly important for the P–S bond but comparable to the standard deviation for the P–N and P–C bonds. For the bond angles the correction is negligible.

Table 6. *Bond lengths* (Å) *and bond angles* (°) *with estimated standard deviations*

(*a*) Bond lengths from the least-squares refinement			
P–N	1·688 (4)	P–C(1)	1·791 (5)
P–N′	1·690 (4)		
		C(1)–C(2)	1·403 (6)
P–S	1·917 (2)	C(2)–C(3)	1·378 (8)
		C(3)–C(4)	1·373 (9)
N–C(7)	1·454 (7)	C(4)–C(5)	1·382 (9)
		C(5)–C(6)	1·383 (8)
C(7)–C(8)	1·450 (10)	C(6)–C(1)	1·375 (8)
		Mean	1·382 (11)
(*b*) Corrected for molecular oscillations			
P–N	1·693 (4)	P–C(1)	1·797 (5)
P–N′	1·696 (4)		
Mean	1·695 (5)*		
		N–C(7)	1·457 (7)
P–S	1·922 (4)*		
(*c*) Bond angles			
N–P–N′	84·5 (3)	P–N–C(7)	128·8 (3)
P–N–P′	95·0 (3)	P′–N–C(7)	129·2 (3)
S–P–C(1)	113·4 (2)	P–C(1)–C(2)	119·7 (4)
		P–C(1)–C(6)	121·6 (4)
N–P–S	120·3 (2)		
N′–P–S	118·5 (2)	C(1)–C(2)–C(3)	119·7 (5)
		C(2)–C(3)–C(4)	121·1 (5)
N–P–C(1)	107·3 (2)	C(3)–C(4)–C(5)	119·4 (6)
N′–P–C(1)	109·3 (2)	C(4)–C(5)–C(6)	119·9 (6)
		C(5)–C(6)–C(1)	121·1 (5)
N–C(7)–C(8)	113·4 (6)	C(6)–C(1)–C(2)	118·7 (5)

* These standard deviations have been enlarged to allow for possible error in the unit-cell parameters.

Table 7. *Root-mean-square amplitudes of thermal vibration* (Å) *along the principal axes of the vibration ellipsoids*

The direction of each principal axis is specified by the angles it makes with the orthogonal axes *a*′, *b*, and *c*.

		a′	*b*	*c*			*a*′	*b*	*c*
S	0·281	35°	73°	61°	C(4)	0·334	22	69	85
	0·229	119	36	71		0·275	82	124	36
	0·174	107	120	36		0·203	110	42	55
P	0·219	45	48	77	C(5)	0·374	21	69	94
	0·190	49	138	83		0·247	96	62	28
	0·153	104	94	15		0·217	110	36	118
N	0·239	92	8	82	C(6)	0·341	17	73	87
	0·201	4	88	87		0·223	106	17	96
	0·169	93	98	9		0·203	95	85	7
C(1)	0·242	36	58	75	C(7)	0·324	108	21	80
	0·199	118	32	105		0·236	40	69	122
	0·173	111	85	21		0·190	56	89	34
C(2)	0·277	30	66	72	C(8)	0·403	100	25	68
	0·229	111	24	101		0·311	137	112	55
	0·167	111	86	21		0·196	48	100	43
C(3)	0·307	16	83	76					
	0·270	91	24	114					
	0·199	106	67	28					

Discussion

Molecular geometry

The isomer of 1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane with melting point 137°C has the *cis* configuration as proposed by Flint *et al.* (1971). The molecules possess exact C_2 symmetry but the phosphazane ring is significantly non-planar [see Table 9, plane (i)]. There is a dihedral angle of 11·5° between the two halves of the ring which meet in the P···P line and of 10·5° between the halves which meet in the N···N line (the difference arises from the inequality of the bond angles at the phosphorus and nitrogen atoms). The torsion angles of the ring bonds are all 7·8°, the symmetry of the ring being $C_{2v}(mm2)$. In contrast the phosphazane ring in the *trans* isomer is planar (Bullen, Rutherford & Tucker, 1973), as are the rings in *trans*-[NMeP(S)Ph]$_2$ (Ibrahim *et al.*, 1971) and *trans*-[NPhP(S)Ph]$_2$ (Peterson & Wagner, 1973). The (B–N)$_2$ ring in [Cl$_2$BNMe$_2$]$_2$ is also planar (Hess, 1963) but non-planar four-membered rings are known for (C–C)$_2$ in cyclobutane (Dunitz & Schomaker, 1952) and its derivatives (Owen & Hoard, 1951; Le-

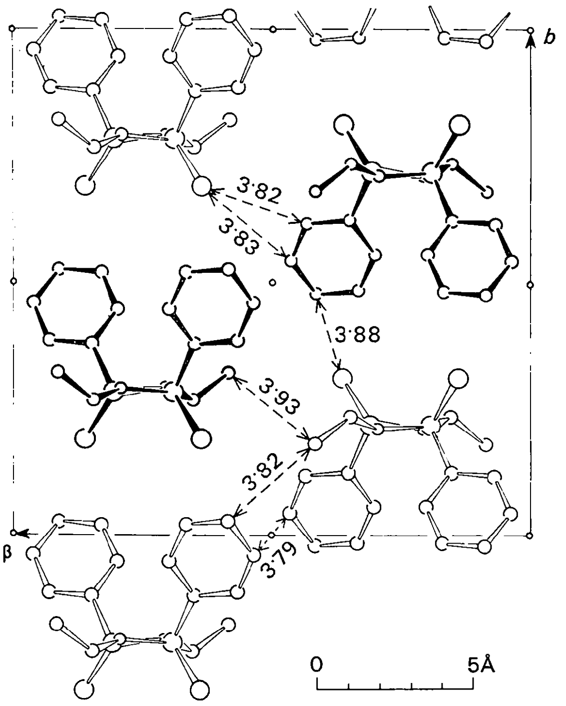


Fig. 2. Projection of the structure down a showing intermolecular S···C and C···C distances (Å). The lightly shaded molecules are at a height $x=0$ and the heavily shaded molecules at $x=\frac{1}{2}$.

Table 8. *Translational* (**T**, Å^2) *and librational* (**ω**, deg^2) *tensors for the central part of the molecule*

See text for definition of the axial system; the origin of **ω** is at (0, 0·196, 0·250).

$$\mathbf{T}=\begin{pmatrix} 0{\cdot}031\ (3) & -0{\cdot}006\ (3) & 0 \\ & 0{\cdot}033\ (3) & 0 \\ & & 0{\cdot}043\ (4) \end{pmatrix} \qquad \boldsymbol{\omega}=\begin{pmatrix} 27\ (3) & 0\ (3) & 0 \\ & 4\ (3) & 0 \\ & & 10\ (3) \end{pmatrix}$$

Table 9. *Equations of mean planes through sets of atoms and distances* (Å) *of atoms from the plane (in square brackets)*

Coordinates in Å are referred to orthogonal axes a', b, and c.

Plane (i): P, N, P′, N′ $Y=3{\cdot}464$
[P, P′ 0·057; N, N′ −0·057]

Plane (ii): P, N, P′, C(7) $-0{\cdot}082X+0{\cdot}995Y-0{\cdot}053Z=3{\cdot}234$
[P, P′ 0·049; N −0·175, C(7) 0·077]

Plane (iii): C(1)–C(6) $0{\cdot}947X+0{\cdot}320Y+0{\cdot}040Z=1{\cdot}878$
[C(1) 0·001, C(2) 0·011, C(3) −0·018, C(4) 0·012, C(5) 0·000, C(6) −0·006, P 0·020]

maire & Livingston, 1952) and for (P–B)$_2$ in [(Ph$_2$P)BI$_2$]$_2$ (Bullen & Mallinson, 1972). It is presumed that these rings are bent in order to allow greater clearance between the exocyclic atoms or groups, and this is probably also the reason for the bending in *cis*-[NEtP(S)Ph]$_2$, since with a planar ring the two phenyl rings would come closer together. (Close contact between the phenyl rings is also relieved by a twist about the P–C bond, see below.) In the *trans*-cyclodiphosphazanes the phenyl groups lie on opposite sides of the ring, so allowing it to be planar.

The molecular dimensions of *cis*- and *trans*-[NEtP(S)Ph]$_2$, compared in Table 10, are for the most part very similar. The comments on the P–N, P–S, and P–C bond lengths and on the coordination of the nitrogen and phosphorus atoms made in discussion of *trans*-[NEtP(S)Ph]$_2$ (Bullen, Rutherford & Tucker, 1973) apply also to the *cis* isomer. The C–C bond in the ethyl group of the *cis* isomer is surprisingly short and we have no explanation for this. The S–P–C–C torsion angle is not the same for the *cis* and *trans* isomers. The small angle in the *trans* isomer signifies that the phenyl group is almost eclipsed with the P=S bond, a conformation which produces a close intramolecular non-bonded S···C contact. As the eclipsed conformation occurs also in *trans*-[NMeP(S)Ph]$_2$ and *trans*-[NPhP(S)Ph]$_2$ it seems unlikely to have been caused by intermolecular forces (Bullen, Rutherford & Tucker, 1973). The larger twist of the phenyl group in the *cis* isomer is almost certainly caused by repulsion between the two phenyl groups within the molecule: C(6) and C(6′) are only 3·68 Å apart. The conformation of the ethyl group (P–N–C–C torsion angle 144°) is remarkably similar to the conformation in one of the molecules in the *trans* isomer structure.

Table 10. *Molecular dimensions in the two isomers of* [NEtP(S)Ph]$_2$

Bond lengths	*cis*	*trans*
P–N	1·695 (5) Å	1·688 (5) Å
P–S	1·922 (4)	1·928 (4)
P–C	1·797 (5)	1·807 (5)
N–C	1·457 (7)	1·468 (6)
C–C	1·450 (10)	1·503 (9)
Bond angles		
N–P–N′	84·5 (3)°	83·3 (2)°
P–N–P′	95·0 (3)	96·8 (2)
P–N–C	129·0 (2)	129·0 (3)
S–P–C	113·4 (2)	113·5 (2)
Torsion angles		
S–P–C–C	35°	12°
P–N–C–C	144	80, 145

Intermolecular distances

The arrangement of the molecules in the unit cell is shown in Fig. 2. The molecular packing is controlled mainly by close S···C and C···C contacts. In addition to those marked in Fig. 2, there are close contacts between molecules separated by the a translation: S···C(7′) $(1+x, y, z)$ 3·95, C(8)···C(2′) $(1+x, y, z)$ 3·56, and C(8)···C(3′) $(1+x, y, z)$ 3·77 Å. Four of the five C···C contacts quoted involve the methyl carbon atom C(8). The shortest S···C contact is the same length (3·82 Å) in the *cis* and *trans* isomers and the distances between ethyl groups are also very similar in the two structures. There is a short S···S distance in *trans*-[NEtP(S)Ph]$_2$ but this type of contact does not occur in the *cis* isomer.

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The Crystal Structure of Histamine Sulphate Monohydrate

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Histamine sulphate crystallizes in the space group $P2_1$ with four formula units, ($C_5H_{11}N_3^{2+}.SO_4^{2-}.H_2O$), in the unit cell of dimensions $a=13{\cdot}124$, $b=7{\cdot}037$, $c=10{\cdot}983$ Å and $\beta=104{\cdot}16°$. The structure was determined by the heavy-atom method and refined by least-squares calculations to $R=0{\cdot}089$. The imidazole ring is protonated and the bond angle C^γ–N^δ–C^ε in the protonated ring is larger than that for an unprotonated one. The skelton of the histamine molecule is roughly planar, although in histamine phosphate the imidazole ring and the aliphatic chain are nearly perpendicular to each other. There is a partial disorder associated with one of the water molecules. The hydrogen-bond scheme is complicated, there being three bifurcated hydrogen bonds and two C–H···O hydrogen bonds.

Introduction

The tertiary structures of many enzymes have been determined by X-ray diffraction, and it has become clear that histidine often plays a key role in the catalytic activity of enzymes. In particular, the imidazole group, the functional side chain of histidine, participates in the activity of many enzymes.

Accurate structure determinations of histidine have been done by Donohue & Caron (1964), Bennett, Davidson, Harding & Morelle (1970) and Madden, McGandy & Seeman (1972). On the other hand, only a few analyses have been reported for the structure of histamine which is obtained from histidine by decarboxylation. The substance has also an important physiological activity. The structure analyses of its phosphate and sulphate were therefore both performed in our laboratory. In this paper only the structure of histamine sulphate will be described, because the structure of the phosphate has already been reported by Veidis, Palenik, Schaffrin & Trotter (1969).

Experimental

The colourless and transparent crystals elongated along the monoclinic *b* axis were obtained by dissolving commercial histamine in 2*N* sulphuric acid. They are hygroscopic and deteriorate quickly on exposure to air: hence all the X-ray data were taken with the crystal coated in a collodion film.

The crystal data are summarized in Table 1. The systematic absence of 0*k*0 reflexions with *k* odd shows that the space group is either $P2_1$ or $P2_1/m$. The $N(z)$ test suggested the space group to be $P2_1$. The *h*0*l* reflexions are weak when $h+l$ is odd, so there exists a pseudo-*n*-glide symmetry.

Table 1. *Crystal data*

$C_5H_{11}N_3^{2+}.SO_4^{2-}.H_2O$
$a=13{\cdot}124$, $b=7{\cdot}037$, $c=10{\cdot}983$ Å, $\beta=104{\cdot}16°$
$V=983{\cdot}5$ Å^3, F.W. 227·24
$D_x=1{\cdot}535$ g cm^{-3} for $Z=4$
D_m (flotation) $=1{\cdot}52$ g cm^{-3}
$\mu=3{\cdot}31$ cm^{-1} (Mo $K\alpha$)
Systematic absence: 0*k*0, $k=2n+1$
Space group: $P2_1$

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