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The Crystal and Molecular Structure of Dimethylaminodifluorophosphine–Tetraborane-8, $(CH_3)_2NPF_2B_4H_8$

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Dimethylaminodifluorophosphine–tetraborane-8, $(CH_3)_2NPF_2B_4H_8$ (mp −18°), crystallizes in space group $P2_1/n$ with four formula units in a cell of dimensions $a = 11.610$ (12) Å, $b = 12.046$ (12) Å, $c = 6.773$ (10) Å, and $\beta = 93° 32'$ (8′) at −75°. The structure has been determined and refined to $R = 0.078$, using 1190 photographic, visually estimated X-ray data. The B_4H_8 group resembles a B_4H_{10} molecule but lacks two bridge hydrogens. It is bonded to the phosphorus atom of the $(CH_3)_2NPF_2$ ligand. The P–B bond length is 1.856 (8) Å. The P–N–C skeleton of the ligand is essentially planar with P–N = 1.593 (6) Å.

Introduction

Tetraborane-8 carbonyl, B_4H_8CO, synthesized by Burg and Spielman in 1959, was the first B_4H_8-containing compound to be isolated.[2] Its formation through reactions of carbon monoxide with either B_5H_{11} or B_4H_{10} indicated that the B_4H_8 group is a cleavage fragment of B_5H_{11} having a structure closely related to that of B_4H_{10}.[3] This view has been substantiated by the results of kinetic studies of the interconversion of tetraborane-10 and pentaborane-11[4] and by the B^{11} nmr spectrum[5] as well as the infrared[3] and Raman spectra of B_4H_8CO.[6] Although free tetraborane-8 has not been isolated, the B_4H_8 group apparently remains intact in the above reactions and in the formation of $B_4H_8PF_3$ from B_5H_{11} and PF_3.[3] The latter reaction is analogous to the reaction of B_5H_{11} with CO. Reversible replacement of PF_3 by CO in $B_4H_8PF_3$ has been observed.[3]

Fleming, Ter Haar, and Parry found that dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, replaces CO in B_4H_8CO forming the new compound $(CH_3)_2NPF_2B_4H_8$.[7] The infrared spectra indicated a close similarity between B_4H_8CO and $(CH_3)_2NPF_2B_4H_8$ and showed the presence of a phosphorus–boron bond in the latter compound.

$(CH_3)_2NPF_2B_4H_8$ is more stable than either B_4H_8CO or $B_4H_8PF_3$ and has the relatively high melting point of −18°. Consequently it afforded the best opportunity for a crystal structure determination aimed at establishing the structure of the B_4H_8 group. The present study was undertaken in order to verify the over-all structure, establish the arrangement of hydrogen atoms in the B_4H_8 group, and obtain accurate molecular parameters.

Experimental Section

Liquid $(CH_3)_2NPF_2B_4H_8$ was sealed in thin-walled Pyrex capillaries of approximately 0.4-mm diameter and mounted on a Buerger precession camera. Crystals were grown by regulating the temperature of a stream of cold nitrogen gas blown over the capillary. Once grown, the crystals were kept at approximately −75°. At temperatures below −100° a phase transition was suggested by the shattering of several crystals.

The crystals belong to the monoclinic space group $P2_1/n$. Unit cell constants, at −75°, with estimated standard deviations were derived from measurement of medium- and high-angle reflections on Mo $K\alpha$ (λ 0.7107 Å) precession photographs of the nets $0kl$, $1kl$, $h0l$, $h1l$, $hk0$, and hkk, all taken at 28° precession angle. The values are $a = 11.610$ (12) Å, $b = 12.046$ (12) Å, $c = 6.773$ (10) Å, and $\beta = 93° 32'$ (8′). The unit cell of volume 945.4 Å^3 contains four formula units. The calculated density of the material is 1.155 g cm^{-3}.

Intensity data were recorded as zero- and upper-level precession photographs using Zr-filtered Mo $K\alpha$ radiation. In order to achieve good coverage of the reciprocal lattice without resorting to excessive inclination of the specimen capillary relative to the incident X-ray beam and, in part, as a result of accidental loss of several crystals, no less than six successively grown crystal specimens were used in the data collection. In each case a single-crystal region was found by a combination of visual observation and examination of diffraction patterns produced by different regions along the capillary. The experimental arrangement and the formation of a thin layer of frost on the outside of the capillary precluded any meaningful measurement of the dimensions of the crystals. However, it is reasonable to assume that the specimens were cylindrical, of approximately 0.4-mm diameter, and that the length of the irradiated crystal sample was about 0.5 mm or less. The scale factors subsequently derived for the various nets indicated that crystals no. 1, 3, 4, 5, and 6 were of approximately equal size, and no. 2 was about 40% smaller. The following reciprocal lattice nets were collected with each of the six crystals: no. 1: $h0l$; no. 2: hkk, $h + n$, $h + l$, l (n = 0–4); no. 3: $0kl$, $1kl$; no. 4: $hk0$; no. 5: hKl (K = 1–6), hkh; no. 6: h, k, $h + n$ (n = 1–7). Three to six exposures were made of each net, ranging from 15 hr to 10 min.

Intensities were evaluated visually by comparison with a scale of timed exposures. Following application of the Lorentz–polarization factor, the 2024 raw F_o^2 values from the 24 reciprocal lattice nets were placed on a common scale by a least-squares procedure which minimizes the departure from zero of the logarithms of all ratios of values for equivalent reflections from different nets.[8] For scaling purposes each of the raw F_o^2 values was given a weight of 3, 2, or 1 depending on its estimated relative accuracy. It was found that 287 independent reflections were observed on two nets, 167 on three, 63 on four, and 6 on five nets. The total number of independent reflections above threshold was 1190.

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[1] National Science Foundation undergraduate research participant, 1963.

[2] A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **81**, 3479 (1959).

[3] J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

[4] J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

[5] A. D. Norman and R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 1143 (1966).

[6] R. C. Taylor, private communication.

[7] M. A. Fleming, Ph.D. Dissertation, University of Michigan, 1963; G. Ter Haar, M. A. Fleming, and R. W. Parry, *J. Am. Chem. Soc.*, **84**, 1767 (1962).

[8] C. E. Nordman, *Acta Cryst.*, **13**, 535 (1960).

TABLE I

FINAL PARAMETERS AND STANDARD DEVIATIONS

(a) Atomic Coordinates

Atom	x	y	z
P	0.4213 (2)	0.2590 (2)	0.4502 (2)
F_1	0.5213 (3)	0.3326 (4)	0.5405 (6)
F_2	0.4989 (4)	0.1747 (4)	0.3463 (7)
N	0.3736 (4)	0.1890 (5)	0.6258 (8)
C_1	0.4508 (9)	0.1209 (10)	0.7540 (15)
C_2	0.2544 (6)	0.1944 (8)	0.6830 (12)
B_1	0.3143 (6)	0.3282 (6)	0.2769 (9)
B_2	0.4167 (8)	0.3886 (8)	0.1120 (13)
B_3	0.2946 (8)	0.4574 (8)	0.1911 (15)
B_4	0.2709 (8)	0.4371 (7)	0.4416 (13)
H_1	0.446 (6)	0.145 (6)	0.884 (12)
H_2	0.427 (7)	0.062 (7)	0.731 (13)
H_3	0.531 (7)	0.125 (6)	0.718 (11)
H_4	0.250 (6)	0.219 (7)	0.784 (12)
H_5	0.202 (6)	0.213 (6)	0.576 (12)
H_6	0.222 (7)	0.124 (7)	0.693 (10)
H_7	0.412 (6)	0.370 (6)	−0.030 (11)
H_8	0.498 (6)	0.390 (6)	0.189 (11)
H_9	0.369 (6)	0.496 (6)	0.114 (11)
H_{10}	0.213 (6)	0.463 (6)	0.086 (11)
H_{11}	0.244 (6)	0.268 (6)	0.240 (10)
H_{12}	0.289 (6)	0.503 (7)	0.331 (12)
H_{13}	0.337 (6)	0.454 (6)	0.559 (11)
H_{14}	0.181 (6)	0.435 (6)	0.484 (10)

(b) Anisotropic Thermal Parameters ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
P	42 (1)	49 (1)	165 (3)	−6 (2)	10 (4)	47 (2)
F_1	50 (3)	114 (4)	280 (11)	−72 (6)	60 (11)	−26 (8)
F_2	95 (4)	91 (4)	322 (12)	77 (6)	58 (11)	180 (11)
N	51 (4)	64 (4)	203 (12)	−11 (6)	75 (12)	37 (11)
C_1	96 (8)	117 (9)	254 (21)	28 (14)	115 (25)	37 (20)
C_2	65 (5)	95 (7)	185 (15)	−33 (10)	−6 (16)	84 (15)
B_1	63 (5)	60 (5)	121 (13)	−1 (8)	9 (13)	26 (13)
B_2	88 (7)	89 (7)	167 (17)	−25 (11)	48 (18)	39 (17)
B_3	65 (6)	69 (6)	321 (26)	−5 (11)	29 (21)	11 (20)
B_4	84 (7)	61 (6)	234 (19)	25 (11)	−45 (18)	31 (19)

Structure Determination

A trial structure was deduced by examining the three-dimensional Patterson function. Initially a consistent set of P–P vectors was found. These vectors required the phosphorus atoms to lie at or near $y = 0.25$ and 0.75 and left a twofold ambiguity in their x and z coordinates. Additional peaks could be interpreted as intra- and intermolecular P–F or P–N vectors. Several alternative sets of coordinates were now considered for the four phosphorus, eight fluorine, and four nitrogen atoms in the unit cell. For each set the Patterson function was examined at the points of all P–P, P–F, P–N, F–F vectors. The best-fitting set was subsequently found to be the correct one.

Following diagonal least-squares refinement of the P, F, and N coordinates, a difference Fourier synthesis was computed, and the carbon atoms as well as some of the boron atoms were found. Further least-squares refinement and another difference Fourier located the remaining boron atoms. All of the P, F, N, and B parameters were now refined using anisotropic temperature factors. A difference Fourier synthesis following this refinement revealed all hydrogen atoms. Diagonal least-squares refinement, using isotropic thermal parameters for the hydrogen atoms, resulted in $R = 0.078$ for the 1190 observed reflections. Form factors given in ref 9 were used for all atoms. Hughes' weighting scheme was used in all refinements; *i.e.*, $\sqrt{w} = 4F_{\min}/F_o$ if $F_o > 4F_{\min}$; $\sqrt{w} = 1$ otherwise. Standard deviations of the positional and thermal parameters were estimated by dividing the 1190 observed data into five sets, each uniformly distributed in $(\sin\theta)/\lambda$. Each set was separately subjected to least-squares refinement, and the standard deviation was estimated from the spread of the resulting values for each parameter.

A modified version of the ORFLS full-matrix least-squares program subsequently became available to us. The 147-parameter model, with 10 anisotropic and 14 isotropic atoms, was refined through several cycles. The standard deviations estimated from the spread of refinements using partial data were found to be in quite good agreement with the least-squares standard deviations. The latter averaged about 20% higher, however, and were therefore preferred and used as the basis for estimates of standard deviations in molecular param-

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(9) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

h	k	l	F_o	F_c
0	0	0	--	3440
0	0	2	84	84
0	0	8	71	-58
0	1	3	376	368
0	1	4	148	143
0	1	6	156	164
0	2	1	678	628
0	2	2	240	-234
0	2	3	157	-151
0	2	7	71	-58
0	3	2	245	-248
0	3	3	342	-368
0	3	4	175	-174
0	3	5	93	-90
0	3	6	112	-113
0	3	7	78	75
0	4	2	282	290
0	4	3	97	104
0	4	8	84	-80
0	5	2	142	157
0	5	3	237	224
0	5	4	365	398
0	5	6	115	115
0	5	8	58	54
0	6	0	131	111
0	6	1	104	110
0	6	3	92	92
0	6	4	76	-84
0	6	6	69	61
0	6	7	77	71
0	6	8	51	50
0	7	1	84	-71
0	7	2	138	-131
0	7	3	125	-125
0	7	4	174	-197
0	7	5	29	23
0	7	6	87	-113
0	8	0	74	-49
0	8	1	90	-89
0	8	2	127	132
0	8	3	144	-137
0	8	4	74	79
0	8	6	79	-65
0	8	7	39	-44
0	9	2	118	119
0	9	4	86	94
0	9	6	89	54
0	10	0	137	-149
0	10	1	94	72
0	10	2	149	-139
0	10	3	62	66
0	10	4	66	-77
0	11	1	118	-119
0	11	2	136	-150
0	11	6	92	-55
0	12	0	120	112
0	12	2	93	96
0	12	3	64	-62
0	12	5	84	-64
0	13	1	107	127
0	14	0	117	-122
1	0	-5	233	247
1	0	-3	241	251
1	0	-1	1021	1021
1	0	1	765	778
1	0	5	154	-147
1	0	7	91	-83
1	1	-7	107	-132
1	1	-4	75	53
1	1	-3	253	-252
1	1	-2	348	347
1	1	-1	266	278
1	1	1	590	574
1	1	2	234	219
1	1	3	105	112
1	1	5	89	92
1	2	-5	152	-159
1	2	-4	59	63
1	2	-3	64	-65
1	2	-2	402	398
1	2	-1	564	-472
1	2	0	92	79
1	2	1	1032	-986
1	2	2	192	-183
1	2	3	61	-56
1	2	4	41	35
1	2	5	133	141
1	2	7	69	49
1	3	-7	89	95
1	3	-5	205	216
1	3	-4	91	-95
1	3	-3	203	182
1	3	-2	665	-638
1	3	0	130	122
1	3	1	391	-380
1	3	2	110	-118
1	3	4	261	-247
1	3	5	209	-224
1	3	6	82	78
1	3	7	55	-61
1	4	-5	64	54
1	4	-4	82	-90
1	4	-3	199	193
1	4	-1	420	353
1	4	0	483	442
1	4	1	198	173
1	4	2	120	123
1	4	3	58	45
1	4	4	105	-108
1	4	5	124	-126
1	4	6	64	54
1	4	7	79	-81
1	5	-7	93	-94
1	5	-6	46	-32
1	5	-5	278	-285
1	5	-4	189	180
1	5	-2	263	268
1	5	-1	140	119
1	5	1	298	273
1	5	2	100	-105
1	5	3	452	424
1	5	4	234	240
1	5	5	176	170
1	5	7	45	54
1	6	-6	60	-47
1	6	-3	368	-361
1	6	-2	74	-69
1	6	0	74	55
1	6	1	92	86
1	6	2	145	139
1	6	4	132	139
1	6	7	92	97
1	7	-7	51	59
1	7	-5	102	120
1	7	-4	96	-98
1	7	-3	163	159
1	7	-2	93	-101
1	7	-1	35	-47
1	7	0	52	-48
1	7	2	88	98
1	7	3	353	-370
1	7	5	128	-138
1	8	-7	42	-29
1	8	-6	78	71
1	8	-4	76	61
1	8	-3	260	249
1	8	-1	77	55
1	8	1	44	-35
1	8	2	216	-218
1	8	6	46	-53
1	8	7	68	-61
1	9	-5	92	-99
1	9	-4	61	-73
1	9	0	93	98
1	9	3	223	215
1	9	4	69	-63
1	10	-6	47	-36
1	10	-4	90	-85
1	10	-3	130	-134
1	10	-1	246	-242
1	10	2	93	101
1	10	5	43	43
1	11	0	93	-110
1	11	1	143	-138
1	11	2	87	-80
1	11	3	69	-78
1	11	4	92	91
1	11	5	62	-48
1	12	-4	51	54
1	12	-3	61	43
1	12	-1	157	162
1	12	0	94	-89
1	12	1	97	92
1	12	2	73	-85
1	13	0	80	84
1	13	1	81	71
1	13	3	42	30
1	14	-1	87	-94
1	15	-3	43	26
1	15	0	44	-63
1	15	1	36	-46
2	0	-8	67	48
2	0	-6	189	214
2	0	-4	223	225
2	0	-2	325	330
2	0	0	473	459
2	0	2	341	367
2	0	4	187	-194
2	0	6	231	-240
2	1	-8	82	-76
2	1	-6	91	-103
2	1	-5	57	56
2	1	-4	81	83
2	1	-3	102	95
2	1	-2	225	-203
2	1	-1	350	325
2	1	0	997	909
2	1	1	411	-389
2	1	2	366	374
2	1	3	46	31
2	1	4	83	-76
2	2	-6	150	-164
2	2	-5	52	55
2	2	-4	197	-190
2	2	-3	211	211
2	2	-2	579	-550
2	2	-1	118	116
2	2	0	619	-557
2	2	1	468	-470
2	2	2	234	-224
2	2	3	71	-75
2	2	4	152	166
2	2	5	54	55
2	2	6	159	170
2	2	7	92	-106
2	2	8	47	61
2	3	-8	90	87
2	3	-7	48	48
2	3	-6	84	93
2	3	-5	76	-55
2	3	-4	120	120
2	3	-3	388	-360
2	3	-1	518	-422
2	3	0	167	-163
2	3	1	58	51
2	3	2	451	-486
2	3	3	142	-144
2	3	4	196	-196
2	3	6	49	-60
2	4	-6	58	60
2	4	-4	248	252
2	4	-2	420	366
2	4	-1	290	-264
2	4	0	304	-273
2	4	1	397	378
2	4	2	54	52
2	4	4	169	-175
2	4	5	106	-97
2	4	6	71	-75
2	4	7	40	44
2	4	8	46	-57
2	5	-8	71	-76
2	5	-6	91	-108
2	5	-5	62	44
2	5	-4	82	-91
2	5	-3	184	180
2	5	-2	212	179
2	5	-1	305	274
2	5	0	202	197
2	5	2	327	293
2	5	4	206	200
2	5	6	85	86
2	5	7	44	-39
2	5	8	38	-49
2	6	-4	231	-232
2	6	-2	93	-88
2	6	-1	292	326
2	6	0	108	84
2	6	1	177	-185
2	6	2	173	174
2	6	3	143	135
2	6	4	121	114
2	6	6	85	84
2	6	8	63	50
2	7	-8	55	45
2	7	-4	168	144
2	7	-2	287	-266
2	7	0	142	-137
2	7	1	61	51
2	7	2	136	-158
2	7	3	132	122
2	7	4	224	-238
2	8	-4	158	153
2	8	-2	171	167
2	8	-1	44	43
2	8	0	192	188
2	8	1	222	-198
2	8	2	88	-101
2	8	3	96	-113
2	8	6	82	-84
2	9	-2	96	89
2	9	-1	46	46
2	9	0	152	123
2	9	3	74	-71
2	9	7	32	-31
2	10	-4	95	-106
2	10	-2	193	-187
2	10	0	69	-69
2	10	1	206	199
2	10	3	90	95
2	10	4	61	61
2	10	5	46	38
2	11	-5	61	-65
2	11	0	93	-80
2	11	1	60	-59
2	11	4	62	-64
2	12	-2	124	120
2	12	-1	78	-76
2	12	0	102	98
2	12	1	107	-125
2	12	4	48	-45
2	13	-3	49	61
2	13	0	99	77
2	13	4	71	51
2	14	-2	64	-58
2	14	0	52	-57
2	14	1	53	67
2	14	4	56	32
2	15	-1	59	-56
2	15	0	72	70
3	0	-7	142	162
3	0	-5	196	189
3	0	-3	337	347
3	0	-1	281	301
3	0	1	277	307
3	0	3	223	-234
3	0	5	96	-86
3	0	7	95	-84
3	1	-5	134	135
3	1	-3	70	71
3	1	-2	188	180
3	1	-1	174	152
3	1	0	271	-249
3	1	1	250	241
3	1	2	335	323
3	1	3	243	244
3	1	5	190	-193
3	2	-7	130	-160
3	2	-5	224	-228
3	2	-4	77	-77
3	2	-3	316	-314
3	2	-2	411	393
3	2	-1	436	-441
3	2	0	185	-180
3	2	1	77	83
3	2	2	295	-284
3	2	3	121	113
3	2	4	101	-88
3	2	5	225	222
3	2	7	99	115
3	3	-7	59	66
3	3	-5	70	83
3	3	-4	191	-182
3	3	-3	185	-188
3	3	-2	350	-326
3	3	-1	339	-300
3	3	1	575	-632
3	3	2	274	-268
3	3	3	182	-187
3	3	4	149	153
3	4	-8	63	62
3	4	-7	70	69
3	4	-5	223	230
3	4	-3	125	125
3	4	-2	383	-329
3	4	0	125	-132
3	4	1	156	-158
3	4	2	377	339
3	4	3	114	-135
3	4	4	118	-109
3	4	5	176	-182
3	4	7	86	-88
3	5	-8	42	22
3	5	-7	64	-67
3	5	-5	93	-79
3	5	-4	161	166
3	5	-3	101	98
3	5	-2	218	243
3	5	-1	361	358
3	5	1	282	281
3	5	2	52	-46
3	5	3	106	90
3	5	4	97	-100
3	5	5	155	149
3	5	7	36	-56
3	6	-5	99	-110
3	6	-4	74	79
3	6	-3	174	-167
3	6	1	196	192
3	6	2	55	-59
3	6	3	187	188
3	6	4	82	65
3	6	5	92	89
3	6	7	68	47
3	7	-7	100	94
3	7	-3	218	-190
3	7	-1	272	-254
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11	2	-1	87	-67
11	2	0	51	-59
11	2	2	142	-132
11	2	3	92	-103
11	3	-6	60	54
11	3	-5	90	80
11	3	-4	58	-59
11	3	-3	154	167
11	3	-1	140	153
11	3	0	88	-90
11	3	1	64	64
11	3	2	50	45
11	4	-6	69	45
11	4	-5	121	-108
11	4	-4	63	61
11	4	-1	47	47
11	4	0	84	84
11	4	1	113	104
11	4	2	61	60
11	4	3	97	100
11	4	5	66	47
11	5	-5	63	-66
11	5	-3	77	-76
11	5	-1	47	-53
11	5	1	102	-106
11	5	3	56	58
11	5	5	41	30
11	6	-5	98	100
11	6	-4	69	-55
11	6	-2	57	-52
11	6	1	85	-89
11	6	3	118	-102
11	6	5	49	-47
11	7	-5	86	54
11	7	-3	111	101
11	8	-5	111	-73
11	8	1	140	112
11	9	-4	66	-56
11	9	0	56	51
11	9	1	80	-59
11	9	2	64	49
11	10	-1	61	-64
11	11	0	22	-25
12	0	-2	76	105
12	0	0	134	132
12	0	2	107	91
12	1	-6	60	-49
12	1	-4	106	-122
12	1	-2	206	-209
12	1	0	89	-96
12	1	4	47	59
12	2	-2	81	-66
12	2	0	142	-152
12	3	-4	116	125
12	3	-3	68	-67
12	3	-2	126	124
12	3	2	64	-49
12	3	4	70	-83
12	4	-5	64	48
12	4	0	96	84
12	4	2	99	98
12	4	3	48	46
12	4	4	59	58
12	5	-4	100	-99
12	5	-2	75	-67
12	5	-1	50	50
12	5	2	44	52
12	5	5	24	-34
12	6	-5	50	-52
12	6	0	125	-97
12	6	2	151	-126
12	7	-4	112	98
12	8	-2	85	76
12	8	0	110	91
13	0	-5	67	52
13	0	-3	97	104
13	0	-1	138	146
13	0	1	107	79
13	1	-5	32	-33
13	1	-3	139	-156
13	1	-1	73	-82
13	1	3	65	75
13	2	-3	83	-85
13	2	-1	103	-119
13	3	-5	67	72
13	3	-3	72	70
13	3	3	74	-70
13	4	-4	69	50
13	4	-3	54	63
13	4	-1	74	69
13	4	1	102	120
13	5	-5	102	-105
13	5	-3	74	-48
13	5	-2	44	48
13	5	1	44	62
13	5	3	66	67
13	6	-4	70	-56
13	6	-3	74	-64
13	6	-1	75	-84
13	6	1	95	-97
13	6	3	50	-51
13	8	-1	93	77
14	0	-4	59	65
14	0	-2	130	152
14	0	0	89	76
14	1	-4	35	-41
14	1	2	69	77
14	2	-4	63	-69
14	2	-2	115	-122
14	3	2	58	-71
14	4	-4	71	66
14	4	-2	73	83
14	4	0	75	70
14	5	-5	30	27
14	5	0	84	79
14	5	2	68	81
14	6	-4	56	-58
14	6	-2	50	-57
14	6	-1	42	44
14	6	0	83	-72
15	0	-1	114	91
15	1	1	46	46
15	2	-1	75	-72
15	3	-1	59	-63
15	4	-1	43	42
15	5	-1	78	81
15	5	1	68	82
15	6	-1	45	-36

eters. As the standard deviations of the individual isotropic hydrogen atom thermal parameters were very large, averaging 1.9 Å^2, the hydrogen atom B's were replaced by the constant value 4.0 Å^2. The remaining 133 parameters were further refined, giving a final R value of 0.078 and a weighted R of 0.107.

The atomic coordinates and their least-squares standard deviations are given in Table I(a) and the thermal parameters for the nonhydrogen atoms in Table I(b). The latter are the parameters β_{ij} in a temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{31}lh)]$. The observed and final calculated structure factors are listed in Table II. Of the 193 F_c values corresponding to unobserved reflections with $(\sin\theta)/\lambda < 0.5$, 17 were found to exceed their assigned threshold values, 2 to exceed $1.5F_{\min}$, and none to exceed $1.8F_{\min}$. The bond distances given in Table III include thermal motion corrections ranging from +0.004 and +0.008 Å for P–B$_1$ and P–N to +0.026 and +0.031 Å for P–F$_1$ and P–F$_2$. These corrections were computed assuming "riding" motion.[10] The uncertainty regarding the exact mechanics of the thermal motion suggests that the least-squares standard deviations in Table III should be regarded as low estimates.

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Table III

Intramolecular Distances and Angles

(a) Bond Distances, Å

$P-B_1$	1.856 (8)	B_1-B_3	1.687 (12)
B_1-B_2	1.844 (11)	B_2-B_3	1.759 (13)
B_1-B_4	1.826 (11)	B_3-B_4	1.753 (14)

B–H (av, regular) 1.08 (0.98–1.15)
B–H (av, bridge) 1.19 (1.10–1.40)

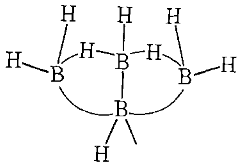
$P-F_1$	1.581 (4)	$N-C_1$	1.483 (13)
$P-F_2$	1.586 (5)	$N-C_2$	1.470 (9)
P–N	1.593 (6)	C–H	0.8–1.0

(b) Angles, Deg

$B_1-B_2-B_3$	55.6 (5)	F_1-P-B_1	116.6 (3)
$B_1-B_4-B_3$	55.9 (5)	F_2-P-B_1	113.1 (3)
$B_2-B_3-B_4$	114.1 (7)	F_1-P-F_2	96.4 (3)
$B_2-B_1-B_4$	107.6 (6)	F_1-P-N	107.1 (3)
$P-B_1-B_2$	97.4 (5)	F_2-P-N	103.3 (3)
$P-B_1-B_4$	97.8 (4)	$P-N-C_1$	121.0 (5)
$P-B_1-B_3$	135.2 (5)	$P-N-C_2$	123.7 (5)
$N-P-B_1$	117.6 (3)	C_1-N-C_2	115.1 (6)

Discussion

Figure 1 shows the electron density distribution in a $(CH_3)_2NPF_2B_4H_8$ molecule viewed along the crystallographic *a* axis and a schematic representation of the same molecule, including thermal motion ellipsoids for the nonhydrogen atoms. The B_4H_8 group is in effect a tetraborane-10 molecule with two bridge hydrogens missing on the same "long" side of the molecule. Thus, the lengthwise mirror plane of B_4H_{10} is destroyed. The perpendicular mirror plane, through B_1 and B_3 bisecting the line $B_2 \cdots B_4$, is present in the B_4H_8 group, within experimental error. The phosphorus atom of $(CH_3)_2NPF_2$ lies in this mirror plane, and is bonded to B_1 on the concave side of B_4H_8. The geometry of the B_4H_8 group supports the type 2112 bonding scheme



which was first proposed by Dupont and Schaeffer[4] on the basis of Lipscomb's topological theory.

The relative orientation of the two ligands about the $P-B_1$ bond is apparently determined by several close nonbonded contacts which are shown in Figure 1. The dihedral angle between the planes B_3B_1P and B_1PN is 52°. At this orientation one of the fluorine atoms (F_1) fits between two terminal hydrogen atoms (H_8 and H_{13}) of B_4H_8, while prohibitively close approaches between other atom pairs are avoided.

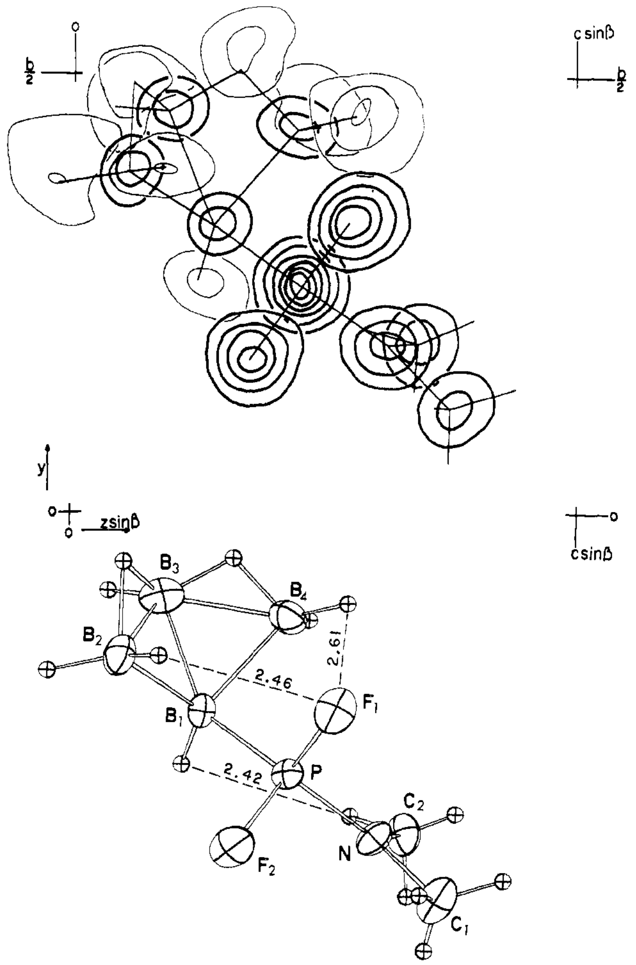


Figure 1.—Top: Electron density distribution in the $(CH_3)_2NPF_2B_4H_8$ molecule. Heavy contours are at intervals of $5\ e^{-}\ \mathrm{\AA}^{-3}$ (P) or $2.5\ e^{-}\ \mathrm{\AA}^{-3}$ (others). Light contours showing the hydrogen atoms as given by a difference Fourier synthesis are at intervals of $0.25\ e^{-}\ \mathrm{\AA}^{-3}$. Zero contour omitted in all cases. Methyl hydrogens are omitted for clarity. Bottom: ORTEP drawing of the same molecule with 25% thermal motion ellipsoids shown for the heavy atoms. Close nonbonded contacts between the two ligands are indicated.

A comparison of the geometry of the B_4H_8 group with B_4H_{10}[11] shows differences which may be accounted for in terms of the nonbonded repulsion of F_1. The dihedral angle between the two boron triangles $B_1B_2B_3$ and $B_1B_3B_4$ is 137° in B_4H_8 compared to 118° in B_4H_{10}. The bridged bonds B_2-B_3 and B_3-B_4 (Table III) are significantly shorter than the values 1.836–1.849 Å found for the four bridged bonds in B_4H_{10}. The phosphorus–boron distance 1.856 (8) Å is slightly but probably not significantly shorter than the P–B bond in $(H_2N)_3PBH_3$, which is 1.887 (13) Å.[8]

The most noteworthy feature of the $(CH_3)_2NPF_2$ ligand is the shortness of the P–N bond and the planarity of the bonds surrounding the nitrogen atom. The mean deviation of the atoms P, N, C_1, and C_2 from the least-squares plane is only 0.015 Å or slightly more than twice the average standard deviation of the atom position. Consequently it cannot be concluded with any certainty that the group is nonplanar.

The phosphorus–nitrogen distance in the $H_3NPO_3^-$ ion is 1.769 (19) Å; this value is usually quoted as the length of a single P–N bond.[12] Most bonds between phosphorus and 3-coordinated nitrogen are shorter. Examples are 1.653 Å in $(H_2N)_3PBH_3$ (average of three

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bonds),[8] 1.67–1.71 Å in $Na_3(HNPO_2)_3 \cdot 4H_2O$,[13] 1.671 and 1.686 Å in $[NP(N(CH_3)_2)_2]_4$,[14] 1.66–1.72 Å in $[CH_3NPO(OCH_3)]_3$ (six independent bonds),[15] and 1.63 and 1.77 in $(CH_3NPCl_3)_2$.[16] The last of these involves 5-coordinated phosphorus; the others involve 4-coordinated phosphorus, as in $(CH_3)_2NPF_2B_4H_8$. The value 1.593 Å found in the present study is shorter than any of these. This parallels the observation in the phosphazenes, $(NPX_2)_n$, $n = 3$ or 4, where P–N bonds involving fluorine-substituted phosphorus tend to be particularly short.[17]

With regard to the configuration at the nitrogen atom only two of the earlier studies afford a meaningful comparison. Of the two independent exocyclic P–N-$(CH_3)_2$ groups in $[NP(N(CH_3)_2)_2]_4$, one is nearly planar (angle sum 358.5°) with P–N = 1.671 (10) Å and the other is distinctly puckered (angle sum 349.5°) with P–N = 1.686 (10) Å.[14] The preliminary study[15] of $[CH_3NPO(OCH_3)]_3$ finds the three crystallographically independent nitrogen atoms essentially planar. Considering the shortness of the P–N bond in $(CH_3)_2NPF_2B_4H_8$, the planarity of its nitrogen atom is in complete agreement with these results.

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The Crystal Structure of Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$

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Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$ (mp −87°), crystallizes with four formula units in an orthorhombic cell with a = 10.808 (12) Å, b = 7.601 (7) Å, and c = 6.259 (6) Å at −110°. A total of 458 photographically recorded and visually evaluated X-ray data were used to determine the structure, which has been refined to R = 0.069. A space group ambiguity was resolved in favor of Pnma following least-squares refinement in both Pnma and $Pn2_1a$ and consideration of the effect of a slight scaling error in the weakest observed reflections. The molecule possesses mirror symmetry with the planar P–N–C skeleton lying in a crystallographic mirror plane. Bond lengths and standard deviations are P–N = 1.628 (5), P–F = 1.610 (4), and C–N = 1.460 (9) and 1.485 (8) Å.

Introduction

Dimethylaminodifluorophosphine was first synthesized by Kodama and Parry,[2] and independently by Nöth and Vetter,[3] Cavell,[4] and Schmutzler.[5] It is a colorless liquid with a normal boiling point of about 50°. Extensive studies of the coordination chemistry of $(CH_3)_2NPF_2$ by Fleming, Ter Haar, and Parry[6] established that the compound is an excellent coordinating ligand with a base strength intermediate between PF_3 and $N(CH_3)_3$. Their results suggested that the ligand is capable of coordinating through the nitrogen atom as well as through the phosphorus atom, depending on the nature of the electron acceptor. $(CH_3)_2NPF_2$ was found to form a stable 1:1 adduct with B_4H_8, presumably involving a phosphorus–boron bond. An X-ray crystal structure determination of this adduct, $(CH_3)_2NPF_2B_4H_8$, was subsequently undertaken.[7] The result confirmed the coordination of the B_4H_8 group to the phosphorus atoms of the ligand. It also revealed that the phosphorus–nitrogen bond in the coordinated ligand is unusually short (1.593 Å) and that the phosphorus, nitrogen, and two carbon atoms are essentially coplanar. This configuration was unexpected; at the time the present investigation was undertaken there was little, if any, precedent for coplanar bonds about three-coordinated nitrogen bonded to phosphorus. A complementary X-ray study of the structure of the free $(CH_3)_2NPF_2$ ligand was consequently judged desirable.

Experimental Section

$(CH_3)_2NPF_2$ melts at −87° and is sensitive to moisture. Accordingly, samples were vacuum distilled into thin-walled Pyrex capillaries of approximately 0.4-mm diameter, which were subsequently sealed. Crystals were grown with the capillary mounted on a Buerger precession camera and cooled with a stream of cold nitrogen gas. The X-ray work was done with the speci-

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