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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men kept at approximately −110°. Zr-filtered Mo Kα radiation (λ 0.7107 Å) was used.

The crystals are orthorhombic with a = 10.808 (12) Å, b = 7.601 (7) Å, and c = 6.259 (6) Å. The unit cell volume is 514.2 Å^3. With four molecules per cell the calculated density is 1.460 g cm^{-3}. Systematic absences of $hk0$ for h odd and of $0kl$ for $k + l$ odd correspond to the space groups Pn2$_1$a (no. 33) or Pnma (no. 62). The general positions in the former are fourfold and in the latter are eightfold. It follows that crystallographically demanded symmetry must be present in the molecule, if Pnma is the correct space group. Of the two alternatives allowed by Pnma, a center of symmetry and a mirror plane, only the latter is chemically reasonable.

Of several consecutive crystals grown and examined, three were chosen for collection of intensity data. The choice was made so as to afford good coverage of the reciprocal lattice while allowing the specimen capillary to remain roughly perpendicular to the incident X-ray beam. Visual observation of the contents of the capillary was made difficult by the unavoidable frosting. It is reasonable to assume, however, that the solid sample filled the capillary and that the effective length of the irradiated specimens was about 0.5 mm. The fact that the three crystals were effectively equal in size was borne out by the subsequent scaling of the data.

The first crystal was used to obtain Mo Kα precession photographs of the $h0l$, $h1l$, and $0kl$ nets; the second was used for hkL (L = 0–4), $h2l$, and $h3l$; and the third was used for Hkl (H = 1–4). The precession angle was 26° for zero-level nets and successively less for upper-level nets. Each net was exposed for a series of periods differing by a factor of 3 and ranging up to 20 hr.

The intensities were estimated visually. Readings within each net were placed on a common scale according to exposure times. After correction for Lorentz and polarization effects, the different nets were placed on one common scale by a least-squares procedure employing the ratios of the intensities of all reflections observed on two or more intersecting nets.[8] Of the 458 unique reflections of measurable intensity, 182 were observed on two intersecting nets. For scaling purposes the 364 measurements of these 182 reflections were assigned weights of 1, 2, or 3, the lowest weight being given to the weakest reflections, whose relative accuracy could be expected to be lowest. In addition to the 458 observed reflections 154 were judged unobservably weak.

Structure Determination

The approximate structure was readily deduced from the Patterson function. The model was first refined in space group Pn2$_1$a. Following several cycles of diagonal least-squares refinement, the six independent hydrogen atoms were located by a difference Fourier synthesis. The structure was then subjected to full-matrix least-squares refinement using 457 observed reflections, $F(002)$ being omitted as suffering from extinction. The hydrogen form factors were those of Stewart, *et al.*,[9] while those of other atoms were from ref 10. The temperature factors of the nonhydrogen atoms were taken as anisotropic, while those of the hydrogen atoms were assumed isotropic, with B = 3.0 Å^2 held constant. Taking $\sqrt{w} = 1$ when $F_o < 4F_{\min}$, $\sqrt{w} = 4F_{\min}/F_o$ otherwise, this model, with 72 variable parameters, refined to a conventional R of 0.067 and a weighted $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.0848.

It had been clear from the beginning that the structure possessed at least an approximate mirror plane at $y = {}^1/_4$, *i.e.*, that it did not depart greatly from space group Pnma. Not only did the heavy-atom skeleton approximate this symmetry, but also the locations of the hydrogen atoms, as revealed by the Pn2$_1$a difference Fourier, appeared to conform to Pnma symmetry.

Nevertheless several features of the refined Pn2$_1$a structure were in apparent disagreement with Pnma. The carbon–nitrogen plane appeared to be slightly tilted about the phosphorus–nitrogen bond with one of the carbon atoms lying 0.17 Å, or 15σ, from $y = {}^1/_4$. The fluorine atoms were removed from their respective mirror images by 0.15 Å (11σ), and one of their anisotropic thermal parameters, equal by symmetry in Pnma, differed by 10σ. There was no chemically reasonable internal consistency among these distortions.

A full-matrix refinement in Pnma with 44 variable parameters, similar to the Pn2$_1$a refinement in every respect except for symmetry restrictions, led to R = 0.078 and R_2 = 0.0953. The expected R factor ratio[11] for these models, $R_2(\text{Pnma})/R_2(\text{Pn2}_1\text{a}) = \mathcal{R}_{28,385,0.50}$, is 1.034 on the basis of the number of parameters alone. The actual ratio 0.0953/0.0848 = 1.124 would overwhelmingly call for rejection of Pnma as the correct space group, if taken at face value.

Even with due allowance for the unreliability of standard deviation estimates and R factor ratios in cases such as this, where the linear terms in the Taylor's series expansion vanish, the criteria calling for rejection of Pnma appeared too strong to be simply disregarded.

In a further effort to reach an unambiguous space group choice, the dependence of the scale factor on $|F_o|$ was investigated by plotting the ratio $\Sigma|F_o|/\Sigma|F_c|$, of local sums of 60 terms each, as a function of $|F_o|$. For the 44-parameter Pnma structure as well as the 72-parameter Pn2$_1$a structure these plots showed a clear rise above unity for values of $|F_o|$ less than about 2.5$F_{\min}$. The departure from unity was somewhat less pronounced for the Pn2$_1$a than for the Pnma data, reaching about 1.09 and 1.13 for the two sets of calculated structure factors, respectively. This strongly indicated a systematic positive scaling error of up to 25% in the intensities, or F^2 values, of the weakest reflections. The fact that the effect was somewhat less pronounced in the ratios involving the Pn2$_1$a F_c values is not surprising since the smallest F_c's are the most likely ones to increase in magnitude by assuming phase angles differing appreciably from 0 or π, through small, spurious parameter shifts. Similar plots of structure factor ratios as functions of $((\sin\theta)/\lambda)^2$ failed to show significant departures from unity, supporting the conclusion that the source of the behavior was indeed a scaling error introduced in the evaluation of the intensities.

The 72-parameter Pn2$_1$a and 44-parameter Pnma refinements were now repeated using only the 238 $F(hkl)$ values for which $F_o > 2.5F_{\min}$. Despite some oscillation of parameters, the Pn2$_1$a refinement produced a monotonic decrease in R_2. It yielded a model

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[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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whose parameters, expressed in terms of their standard deviations, departed from their Pnma values by less than one-third of the amounts found in the refinement using the complete data. More significantly, the R_2 values for the Pnma and Pn2$_1$a models were 0.0673 and 0.0636, respectively, giving a ratio R_2(Pnma)/R_2(Pn2$_1$a) = 1.058. This is in fact *less* than the expected value $\Re_{28,166,0.50}$ = 1.079, showing that the centric space group cannot be rejected even at the 0.50 level of confidence. On the basis of these results we accept Pnma as the true space group. We also note the extreme sensitivity of the space group assignment to a relatively minor, systematic scale error in the weakest reflections.

To correct for the scaling error, all observed F's less than $2F_{\min}$ were multiplied by 0.89, and those in the range $2F_{\min}$–$2.5F_{\min}$, by 0.94.

Refinement of the 44-parameter model now led to $R = 0.069$ and $R_2 = 0.086$ for the 457 observed reflections included. The final observed and calculated structure factors are listed in Table I. For $(\sin\theta)/\lambda < 0.5$ there were 43 reflections judged unobservably weak. All but one of these have F_c values less than their respective threshold values. For the sole exception (124) F_c exceeds $F_{\text{threshold}}$ by 4%.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	0	--	2320	2	3	4	49	53	4	4	1	57	53	6	5	0	71	62	9	2	3	138	-134
0	0	4	314	310	2	3	5	93	-91	4	4	2	298	304	6	5	2	57	70	9	2	4	79	-74
0	0	6	67	-72	2	3	7	78	-75	4	4	3	235	-213	6	5	3	51	55	9	3	2	49	38
0	1	1	256	-228	2	3	8	42	45	4	4	4	55	50	6	6	0	169	174	9	3	4	113	124
0	1	5	257	-247	2	4	0	102	89	4	4	5	55	-58	6	6	1	124	-120	9	3	5	68	-60
0	1	7	69	-75	2	4	1	218	-209	4	4	7	56	-60	6	6	2	79	75	9	3	6	52	44
0	2	0	761	-946	2	4	2	320	-336	4	5	0	53	-58	6	7	0	120	-121	9	4	1	177	179
0	2	2	591	-514	2	4	3	65	59	4	5	1	120	-118	6	8	0	112	-112	9	4	3	132	126
0	2	4	58	-77	2	4	6	41	-24	4	5	2	106	-96	6	8	2	58	-47	9	4	4	55	65
0	2	8	93	82	2	5	0	193	164	4	5	3	160	177	6	9	2	43	44	9	5	2	69	-64
0	3	1	471	-451	2	5	1	68	61	4	5	5	103	-122	7	0	1	243	-249	9	6	1	150	-148
0	3	3	379	398	2	5	2	49	45	4	6	0	205	-206	7	0	2	90	-70	9	6	3	51	-49
0	3	5	91	99	2	5	3	115	129	4	6	1	171	158	7	0	3	49	-49	9	7	2	51	53
0	3	7	89	84	2	5	5	99	93	4	6	2	100	-100	7	0	4	56	-52	9	8	3	36	45
0	4	0	316	299	2	5	7	46	66	4	6	4	79	-79	7	0	5	43	-36	10	0	0	90	91
0	4	2	462	484	2	6	0	243	242	4	6	4	80	90	7	0	6	117	-96	10	0	1	129	134
0	4	8	80	-79	2	6	3	32	38	4	7	0	127	121	7	1	1	310	-316	10	0	2	92	-95
0	5	3	146	-160	2	6	4	67	77	4	7	1	135	129	7	1	2	119	112	10	0	3	56	55
0	5	5	102	-105	2	7	0	155	-152	4	7	3	65	76	7	1	3	136	-149	10	0	5	72	95
0	6	0	490	-506	2	7	1	161	-147	4	7	4	69	59	7	1	6	103	107	10	1	0	151	152
0	6	2	79	-75	2	7	5	89	-101	4	7	5	87	103	7	2	1	168	164	10	1	2	88	86
0	6	4	128	-113	2	8	0	97	-99	4	8	0	118	103	7	2	2	58	59	10	1	3	98	98
0	7	1	127	123	2	8	2	64	-54	4	8	1	66	-60	7	2	3	159	143	10	1	4	53	50
0	7	5	102	118	2	8	4	57	-48	4	8	2	74	77	7	2	4	70	59	10	2	1	58	-47
0	8	0	230	249	2	9	0	52	40	4	8	3	48	-34	7	2	5	65	-51	10	2	3	102	-93
0	8	2	106	94	2	9	3	54	63	4	8	4	64	53	7	2	6	97	88	10	2	4	60	46
0	9	3	66	-75	2	10	2	75	73	4	8	5	43	-58	7	3	1	253	245	10	2	5	94	-84
0	10	2	92	-103	3	0	1	88	-92	4	9	2	60	-61	7	3	3	138	153	10	3	1	98	-102
1	0	1	378	428	3	0	2	336	-364	4	9	3	54	-72	7	3	4	113	-116	10	3	2	145	-141
1	0	2	362	400	3	0	3	80	68	5	0	1	202	203	7	4	1	122	-120	10	3	5	79	-67
1	0	3	200	195	3	0	4	235	-237	5	0	2	178	185	7	4	2	50	-50	10	4	3	103	97
1	0	4	56	-48	3	0	5	55	-47	5	0	3	58	-50	7	4	3	135	-129	10	4	1	38	-34
1	0	5	46	-33	3	0	6	179	-179	5	0	4	49	38	7	4	4	68	-53	10	4	5	79	60
1	0	6	229	230	3	0	7	68	56	5	0	5	162	163	7	4	5	53	58	10	5	0	67	68
1	1	1	583	546	3	1	1	390	-409	5	0	6	134	128	7	4	6	58	-65	10	5	2	76	83
1	1	2	126	-128	3	1	2	34	30	5	0	7	45	-57	7	5	1	130	-131	10	5	3	48	43
1	1	3	174	163	3	1	3	41	-39	5	1	1	212	200	7	5	2	59	63	10	6	0	39	-36
1	1	4	93	90	3	1	4	41	-28	5	1	2	256	-248	7	5	3	121	-116	10	6	1	61	-60
1	1	5	58	14	3	1	5	153	-175	5	1	3	96	91	7	6	1	129	119	10	6	2	50	53
1	1	6	71	-63	3	1	6	55	47	5	1	4	176	-198	7	6	2	35	17	10	6	3	16	-43
1	1	7	75	-76	3	1	7	52	47	5	1	6	113	-105	7	6	3	45	30	10	7	2	39	-33
1	2	1	294	-289	3	2	3	92	77	5	2	1	125	-126	7	7	1	126	126	10	7	3	43	-31
1	2	2	97	-101	3	2	4	366	368	5	2	2	75	-76	7	7	2	59	-55	11	0	1	132	-111
1	2	3	232	-133	3	2	5	53	-41	5	2	3	97	-93	7	7	3	59	68	11	0	2	45	-33
1	2	4	181	-176	3	2	6	118	90	5	2	4	133	-113	7	8	1	65	-67	11	0	3	48	-46
1	2	5	73	70	3	3	1	184	171	5	2	5	59	-52	7	8	3	48	-44	11	0	4	79	-76
1	2	6	112	-107	3	3	3	235	202	5	2	6	87	-84	8	0	0	101	98	11	1	1	66	-59
1	2	8	39	-59	3	3	4	69	-79	5	3	1	175	-159	8	0	1	175	-173	11	1	2	116	124
1	3	1	313	-296	3	4	2	121	-121	5	3	2	82	78	8	0	2	131	191	11	1	3	65	-60
1	3	3	310	362	3	4	3	66	-80	5	3	4	293	288	8	0	5	139	-135	11	1	4	178	146
1	3	5	117	112	3	4	4	319	-312	5	4	1	113	110	8	1	0	185	-189	11	2	1	107	119
1	4	1	177	158	3	4	6	58	-56	5	4	2	39	38	8	1	2	135	-140	11	2	2	60	55
1	4	3	120	101	3	4	8	54	-57	5	4	5	30	28	8	1	3	93	-101	11	2	3	79	74
1	4	4	185	177	3	5	1	192	173	5	4	6	73	57	8	1	4	94	-100	11	2	4	53	43
1	4	5	69	-63	3	5	2	44	32	5	5	1	169	151	8	1	5	58	-65	11	3	1	66	65
1	4	6	75	67	3	5	3	72	-67	5	5	2	135	-118	8	1	6	46	47	11	3	2	74	-79
1	4	8	72	61	3	5	5	72	-79	5	6	1	111	-114	8	2	0	170	-173	11	3	4	150	-162
1	5	1	273	272	3	6	1	67	50	5	6	2	71	-73	8	2	2	125	-119	11	3	5	37	37
1	5	3	142	135	3	6	2	158	156	5	7	1	106	-104	8	2	3	135	132	11	4	1	100	-97
1	5	6	54	-45	3	6	4	130	133	5	7	2	89	88	8	2	4	37	-57	11	4	2	53	-45
1	6	1	115	-105	3	6	6	73	93	5	7	3	45	-40	8	2	5	102	96	11	4	3	78	-70
1	6	2	130	141	3	7	1	139	140	5	8	1	64	56	8	3	0	207	215	11	5	2	70	75
1	6	3	53	-46	3	7	5	73	78	5	8	3	47	27	8	3	1	88	90	11	5	3	46	-42
1	6	6	121	-118	3	8	2	71	-69	5	9	1	47	52	8	3	2	275	287	11	6	1	80	81
1	7	1	189	-184	3	8	4	108	-111	5	9	3	51	44	8	3	3	33	32	12	0	1	92	-95
1	7	3	57	-61	3	9	1	73	-70	6	0	0	387	-413	8	3	5	89	92	12	0	2	54	59
1	8	1	59	57	3	9	3	58	-53	6	0	1	338	345	8	4	0	153	160	12	0	3	153	-149
1	8	2	52	53	4	0	0	542	574	6	0	2	130	-139	8	4	1	89	83	12	1	0	163	-165
1	8	3	51	43	4	0	1	531	-585	6	0	3	45	-38	8	4	2	79	91	12	1	1	60	57
1	9	1	81	87	4	0	2	80	87	6	0	4	64	-61	8	4	3	145	-146	12	1	2	127	-126
1	9	3	78	83	4	0	3	41	32	6	0	5	153	155	8	4	4	57	58	12	2	0	73	-69
2	0	0	564	-593	4	0	4	178	181	6	1	0	260	257	8	4	5	57	-60	12	2	1	78	72
2	0	2	174	174	4	0	5	181	-191	6	1	1	51	-45	8	5	0	233	-256	12	2	3	144	144
2	0	3	194	-178	4	0	7	40	-44	6	1	2	76	-59	8	5	2	145	-149	12	3	0	113	125
2	0	4	188	-218	4	1	0	303	-282	6	1	3	54	52	8	5	3	53	-53	12	3	2	120	126
2	0	5	56	54	4	1	1	405	-396	6	1	4	91	97	8	6	0	73	-74	12	3	3	47	-41
2	0	6	51	39	4	1	2	38	-41	6	1	5	52	54	8	6	1	59	55	12	3	4	51	60
2	1	0	613	629	4	1	3	182	-195	6	2	0	321	304	8	6	2	94	-101	12	4	0	54	74
2	1	2	93	-101	4	1	4	124	-134	6	2	2	147	146	8	6	3	47	38	12	4	1	55	-50
2	1	3	39	38	4	1	5	205	-221	6	2	3	168	-158	8	7	0	207	218	12	4	3	131	-124
2	1	4	49	38	4	1	7	104	-99	6	2	4	57	59	8	7	2	64	57	12	5	2	95	-96
2	1	5	203	201	4	2	0	180	-181	6	2	5	93	-81	8	7	3	53	49	13	0	1	124	128
2	1	6	55	-44	4	2	1	87	82	6	3	0	148	141	8	8	2	53	52	13	0	2	60	-64
2	1	7	72	73	4	2	3	176	196	6	3	1	90	76	8	8	3	39	-31	13	0	3	65	65
2	2	0	46	-53	4	2	4	101	-99	6	3	2	226	-241	9	0	1	272	278	13	1	2	75	-71
2	2	1	263	266	4	2	5	117	108	6	3	3	57	-64	9	0	3	70	67	13	2	1	109	-114
2	2	2	262	309	4	2	7	67	55	6	3	4	41	34	9	0	4	100	100	13	2	2	45	43
2	2	4	45	40	4	3	0	226	-205	6	3	5	60	-63	9	1	2	113	-104	13	2	3	77	-71
2	3	0	139	-131	4	3	4	45	-50	6	4	0	191	-202	9	1	4	74	-69	13	3	2	51	54
2	3	1	253	236	4	3	5	148	156	6	4	1	79	-79	9	1	5	54	50	13	4	1	99	90
2	3	2	193	-190	4	3	7	78	85	6	4	2	124	-125	9	2	1	230	-226	13	4	3	70	61
2	3	3	295	-327	4	4	0	60	63	6	4	7	54	46	9	2	2	53	-42					

Discussion

The possibility of a slightly puckered P–N–C configuration with disorder about the crystallographic mirror plane can be discounted by considering the anisotropic thermal parameters (Table II). If such a disorder were present, one would expect the mean-square thermal vibration amplitudes perpendicular to the mirror plane to be unusually large for at least some of the four atoms. Since these quantities, $\overline{u}_2^2 = \beta_{22}b^2/2\pi^2$, are no greater than the corresponding mean-square amplitudes in the x and z directions, we conclude that the molecular configuration is planar.

Figure 1 shows an ORTEP drawing of the molecule, with bond distances and angles. The P–F, P–N, N–C$_1$, and N–C$_2$ distances have been corrected for thermal motion by the amounts +0.019, +0.001, +0.008, and +0.016 Å, respectively. These corrections assume "riding" motion[12] and as such are probably conservative. The least-squares standard deviations shown in Figure 1 do not reflect the uncertainty in the implied model for the thermal motion. Hence the standard deviations may be somewhat low.

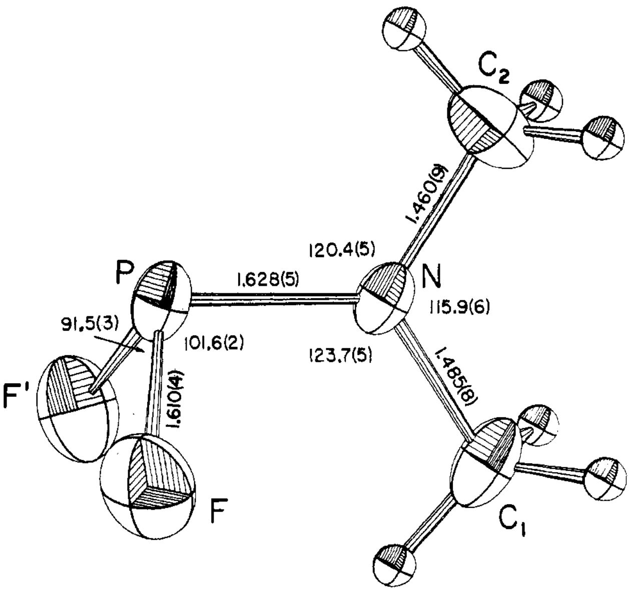

Figure 1.—ORTEP drawing of the $(CH_3)_2NPF_2$ molecule with 50% thermal motion ellipsoids for the nonhydrogen atoms. Bond lengths, in ångströms, and angles, in degrees, are given with standard deviations expressed in units of the last significant figure.

Carbon–hydrogen distances range from 0.94 to 1.03 Å, N–C–H angles from 106 to 112°, and H–C–H angles from 101 to 117°. There are no significant differences within any of the three categories.

The molecular geometry of the free $(CH_3)_2NPF_2$ ligand is very nearly the same as in the B_4H_8 adduct.[7] On forming the adduct the ligand shows a probably significant shortening of both the P–N and P–F bond distances by about 0.03 Å. This is accompanied by an

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(12) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964); W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL Report TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 1964.

TABLE II

FINAL PARAMETERS AND STANDARD DEVIATIONS

(a) Atomic Coordinates

Atom	Position	*x*	*y*	*z*
P	4c	0.2695 (1)	0.2500	0.4553 (3)
F	8d	0.2874 (3)	0.1001 (4)	0.2805 (5)
N	4c	0.4040 (4)	0.2500	0.5727 (8)
C_1	4c	0.5229 (5)	0.2500	0.4565 (14)
C_2	4c	0.4123 (8)	0.2500	0.8029 (11)
H_1	8d	0.523 (5)	0.143 (7)	0.512 (9)
H_2	4c	0.501 (8)	0.2500	0.301 (14)
H_3	8d	0.459 (5)	0.154 (7)	0.854 (8)
H_4	4c	0.327 (8)	0.2500	0.855 (13)

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
P	28 (1)	105 (3)	182 (4)	0	0	−23 (4)
F	90 (3)	139 (6)	257 (9)	−16 (7)	−109 (12)	−79 (8)
N	23 (4)	126 (9)	158 (15)	0	0	2 (10)
C_1	27 (5)	137 (12)	275 (22)	0	0	12 (17)
C_2	87 (8)	150 (14)	130 (16)	0	0	−44 (18)

increase in the bond angles at the phosphorus atom. The F–P–F angle is 91.5 (3)° in the free ligand and 96.4 (3)° in the adduct while the F–P–N angle is 101.6 (2)° in the ligand and 103.3 (3) and 107.1 (3)° in the adduct. The changes in bond distances are supported by an observed increase in P–F stretching frequency in the B_4H_8 adduct relative to the free ligand and a similar although less pronounced effect in the P–N frequency.[13] Comparable changes in geometry, *i.e.*, shortened bonds and increased angles at the phosphorus atom, have been found in virtually all investigated cases of three-coordinated phosphorus upon addition of a fourth neighbor,[14–16] and several models accounting for such changes have been proposed.[17] The closest available parallel to the present system appears to be the pair PF_3 and PF_3-BH_3. A recent accurate microwave determination of the structure of PF_3 by Hirota[18] gives P–F = 1.565 Å and ∠FPF = 96.3°, while another microwave study of PF_3BH_3 by Kuczkowski and Lide[15] gave P–F = 1.538 (8) Å and ∠FPF = 99.8 (10)°. The changes in P–F bond length and FPF angle upon addition of the boron ligand agree very closely with the less accurately determined changes in the present study.

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