$(CF_3)_2PPF_2 \cdot BH_3$ was effected when distillation through the −95° trap was slow.

The vapor density of $(CF_3)_2PPF_2 \cdot BH_3$ also corresponds well with theory (mol wt: calcd, 251.8; found, 253). However, the molecule dissociates easily as evidenced by the observation of appreciable amounts of B_2H_6 and $(CF_3)_2PPF_2$ in the infrared spectra and the lack of a molecular ion in the mass spectrum of $(CF_3)_2PPF_2$ (Figure 1). Other easily dissociated species such as $B_4H_8 \cdot CO$ also show only fragment ions by conventional mass spectrometry.[42]

Instrumentation.—Infrared spectra were obtained with an 87-mm gas cell equipped with CsI windows on either a Beckman IR-10 or a Beckman IR-12. The Raman samples were sealed in capillary tubes and the spectra determined on a SPEX Ramalog 1401 using an argon ion laser. A Consolidated Electrodynamics Model 21-103B operating at 70 eV was used to obtain the mass spectra. The ^1H, ^{19}F, ^{31}P, and ^{11}B nmr spectra were determined with a Varian HR-100 operating at 100.0, 94.1, 40.5, and 32.1 MHz, respectively. A Cary 14 was used to obtain the uv spectra of samples in a 103-mm quartz gas cell.

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The Phosphorus–Phosphorus Bond. III. The Microwave Spectrum, Conformation, and Dipole Moment of Phosphinodifluorophosphine[1]

BY R. L. KUCZKOWSKI,* H. W. SCHILLER, AND R. W. RUDOLPH*

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The rotational spectrum of phosphinodifluorophosphine was assigned with the following rotational constants (MHz): $A = 6916.53$, $B = 3372.94$, $C = 2648.59$ for H_2PPF_2; $A = 6625.56$, $B = 3192.44$, $C = 2522.37$ for D_2PPF_2. The dipole moment was measured as 1.71 ± 0.01 D, with principal axes components $\mu_a = 1.25$ D and $\mu_c = 1.16$ D. From the rotational constants and dipole moment data, the conformation was determined as trans. With the assumption that $d(\mathrm{PH}) = 1.42 \pm 0.01$ Å, the following structural parameters were derived: $d(\mathrm{PP}) = 2.218 \mp 0.038$ Å, $d(\mathrm{PF}) = 1.587 \pm 0.013$ Å, $\angle\mathrm{HPH} = 93.2 \mp 1.0°$, $\angle\mathrm{HPP} = 90.3 \mp 0.4°$, $\angle\mathrm{FPF} = 98.2 \mp 1.2°$, and $\angle\mathrm{FPP} = 97.2 \pm 1.6°$.

Introduction

Structure investigations of diphosphines are of interest because of the possibility of conformational isomerism. Although no precise structural data are available, the infrared and Raman spectra have been interpreted in terms of a gauche configuration for P_2H_4[2,3] and a trans configuration for P_2F_4[4] and P_2Cl_4.[5] Vibrational spectra and X-ray data also confirm the trans symmetry for P_2I_4.[6,7] Vibrational spectra for $(CH_3)_4P_2$ indicated a gauche–trans rotameric mixture in the liquid phase but only the trans form in the solid.[8] A recent electron-diffraction study of gaseous $(CH_3)_4P_2$ indicated that the dihedral angle (ϕ) was 164 ± 23°, measured from the cis configuration[9] ($\phi = 0°$ for cis, 180° for trans). Finally, semiempirical SCF and extended Hückel MO calculations for P_2H_4 and P_2F_4 suggested that the stability of the various conformations decreases in the order gauche > cis > trans.[10]

In the related compounds $F_2PN(CH_3)_2$ and F_2PNH_2, a pyramidal arrangement of neighboring atoms about phosphorus was found; however, the arrangement about the nitrogen was planar and the NX_2 plane bisected the FPF angle.[11,12] PF_2PH_2 has been recently synthesized;[1,13] in view of the above data it was of interest to determine its conformation.

Experimental Section

Apparatus.—The spectra were obtained with a Stark modulated spectrometer which has been described previously.[14] The transitions were measured with a precision of about 0.2 MHz. The absorption cell was cooled with Dry Ice (−78°) for all observations.

Materials.—The H_2PPF_2 was prepared by the reaction of PF_2I and PH_3 and identified by comparison with the reported infrared, nmr, and mass spectra.[1,13] The D_2PPF_2 was made by substituting PD_3 obtained by hydrolysis of calcium phosphide. The synthesis of D_2PPF_2 was confirmed by infrared spectroscopy.

Spectra.—The transitions which were assigned for the two isotopic species are listed in Table I. The rotational constants listed in Table II were obtained by a least-squares fit of the observed transitions. The assignment was based on the Stark effect and the rigid-rotor fit for both species.

In addition to the transitions from H_2PPF_2, absorptions from the decomposition products PF_2H and PF_3 were also noted. A weaker satellite line was found accompanying many of the ground-state lines. This was attributed to a vibrational satellite since the lowest fundamental has been assigned at 209

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TABLE I

OBSERVED AND CALCULATED TRANSITIONS (MHz) FOR H_2PPF_2 AND D_2PPF_2

	H_2PPF_2		D_2PPF_2	
Transition	ν(obsd)	ν(obsd) − ν(calcd)	ν(obsd)	ν(obsd) − ν(calcd)
$1_{10} \rightarrow 2_{20}$	23,498.61	0.33	22,488.05	0.14
$1_{11} \rightarrow 2_{21}$	24,122.66	0.14	23,069.03	−0.11
$2_{11} \rightarrow 3_{21}$	29,183.96	0.12	27,878.03	−0.10
$2_{11} \rightarrow 3_{12}$	19,083.84	0.33		
$2_{02} \rightarrow 3_{12}$	24,176.33	0.40	22,952.08	0.13
$2_{02} \rightarrow 3_{03}$	17,676.40	0.24		
$3_{03} \rightarrow 4_{04}$	23,182.31	0.02	22,050.95	−0.33
$3_{13} \rightarrow 4_{14}$	22,460.91	0.12	21,361.10	−0.50
$3_{12} \rightarrow 4_{13}$	25,306.54	0.20	23,997.77	0.01
$3_{22} \rightarrow 4_{23}$	24,007.90	0.03	22,789.50	−0.37
$3_{21} \rightarrow 4_{22}$	24,910.92	−0.13	23,597.30	−0.05
$4_{04} \rightarrow 5_{05}$	28,505.98	−0.20	27,132.49	0.21
$4_{14} \rightarrow 5_{15}$	27,939.98	−0.02	26,579.98	0.28
$4_{13} \rightarrow 5_{14}$	31,385.29	−0.01	29,779.53	0.04

TABLE II

ROTATIONAL CONSTANTS (MHz), MOMENTS OF INERTIA (AMU Å²), AND SECOND MOMENTS (AMU Å²) FOR H_2PPF_2 AND D_2PPF_2

	H_2PPF_2	D_2PPF_2
A	6916.53	6625.56
B	3372.94	3192.44
C	2648.59	2522.37
I_a	73.0902	76.3001
I_b	149.8784	158.3525
I_c	190.8679	200.4190
P_a	133.8280	141.2357
P_b	57.0398	59.1833
P_c	16.0503	17.1168

cm^{-1};[1] it was not extensively investigated. Attempts were made to identify additional low J lines arising from a second conformation but none was found indicating that another isomeric form is markedly less abundant. The infrared, Raman, and nmr spectra also have offered no evidence suggesting a second rotamer.[1,13]

Dipole Moment.—The Stark shift measurements were made with a precision dc voltage source (Fluke 413B) using the method described by Kirchhoff.[15] The second-order Stark coefficients are listed in Table III. The data were consistent to better than 1%. The effective guide spacing was determined using μ = 0.7152 D for OCS.[16]

Analysis

Selection Rules and Dipole Components.—The symmetry of the conformer can be determined in principle by noting the projections that the total dipole moment makes along the principal axes. For a species with no symmetry such as gauche, the total dipole will have nonzero components for μ_a, μ_b, and μ_c. For a species such as trans with C_s symmetry, there will be two components since the total dipole moment must lie in the symmetry plane. For a species with a C_2 axis such as a planar C_{2v} conformation, only one component will be nonzero. The existence of the dipole components can be determined by the types of transitions observed and by the Stark effect.

The transitions that were assigned in Table I consisted of both μ_a and μ_c types of about equal intensity. The μ_b type transitions were also predicted and a search was made for them. Although a few weak transitions were found at these predicted frequencies, most of the intense lines could not be found and hence no support for b type selection rules was obtained. Since the intensity of a transition is proportional to the dipole component squared, μ_b was estimated to be ≤ 0.1 D.

The Stark effect was also quantitatively investigated in order to place a limit on the magnitude of μ_b, since the frequency shifts ($\Delta\nu$) in the electric field (ϵ) are determined by

$$\Delta\nu/\epsilon^2 = K_a\mu_a^2 + K_b\mu_b^2 + K_c\mu_c^2 \qquad (1)$$

K_a, K_b, and K_c are the second-order perturbation coefficients. These are readily calculated if the rotational constants are known.

The experimental Stark coefficients ($\Delta\nu/\epsilon^2$) which are listed in Table III were fit by a least-squares procedure for the three dipole components giving μ_a^2 = 1.54 D, μ_b^2 = 0.013 D, and μ_c^2 = 1.35 D. The fit for these values is listed under "Calcd I." If μ_b^2 was fixed identical with zero and the least-squares procedure was repeated, then the values obtained were μ_a^2 = 1.55 D and μ_c^2 = 1.36 D. The fit for these values is listed under "Calcd II." Both fits are equally good and are within experimental uncertainty; hence it appears that $\mu_b^2 \leq 0.01$ D. Since the isotope shifts discussed below show that μ_b = 0, we have chosen the second set of dipole components to calculate the total dipole moment. They give $|\mu_a|$ = 1.25 D, $|\mu_c|$ = 1.16 D, and a total dipole moment of 1.71 ± 0.01 D. The values of K_a, etc., have also been listed in Table III to show the sensitivity of the equations to the dipole components.

TABLE III

OBSERVED AND CALCULATED STARK COEFFICIENTS ($10^5 \times$ MHz CM²/V²) AND THE CALCULATED SECOND-ORDER PERTURBATION COEFFICIENTS

			Calcd				
Transition		Obsd	I[a]	II[a]	K_a	K_b	K_c
$2_{02} \rightarrow 3_{12}$	m = 1	1.062	1.062	1.062	−0.0847	0.4127	0.7923
$2_{11} \rightarrow 3_{12}$	m = 1	−0.3476	−0.3493	−0.3504	−0.2650	−0.1503	0.0452
$2_{11} \rightarrow 3_{12}$	m = 2	−1.250	−1.250	−1.250	−0.9742	−0.8838	0.1950
$2_{02} \rightarrow 3_{03}$	m = 0	−0.1548	−0.1531	−0.1544	−0.0990	−0.0004	−0.0004
$3_{22} \rightarrow 4_{23}$	m = 0	0.0823	0.0823	0.0823	0.0218	0.0427	0.0362

[a] Consult text for definition.

The transitions in Table III were selected to ensure that the experimental data could be safely interpreted using second-order perturbation theory. This was necessary since calculations showed that contributions from a possible small value of μ_b in second-order would be comparable to fourth-order corrections to the Stark energy from μ_a and μ_c. Ignoring these higher order corrections could lead to an erroneous conclusion concerning μ_b.[17] The transitions in Table III were selected after comparing the Stark shifts calculated from preliminary values of μ_a and μ_c using eq 1 with

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those calculated by a diagonalization of the Stark energy matrix[18] for J up to 6. Only transitions giving the same Stark shift were retained in Table III. This procedure neglected higher order corrections from μ_b, which upon examination of the form of the fourth-order corrections derived by Kirchhoff[15] is justified if μ_b is small.

In summary, the absence of evidence for μ_b type selection rules indicates that it is certainly small and is probably zero. This strongly suggests that the conformer is not gauche, although it cannot be rigorously eliminated since μ_b could accidentally be close to zero. From an examination of bond dipole arguments, this possibility seems unlikely. Since μ_a and μ_c are both nonzero, structures possessing a C_2 axis are also eliminated. The dipole data are most consistent with a conformer having C_s symmetry.

Isotope Shift.—The moments of inertia for the normal isotopic species do not uniquely determine the symmetry because of the large number of structural parameters. However, the additional data from the D_2PPF_2 species do help to define the symmetry by the following arguments.

(1) The second moments of inertia (Table II) for both isotopic species [$P_a = {}^1/_2(I_b + I_c - I_a)$, etc.] show that P_a, P_b, and P_c changed upon deuteration. This indicates that the conformer cannot have a plane of symmetry containing two hydrogens, thus eliminating a structure analogous to H_2NPF_2.

(2) The differences in moments of inertia [I_a (normal) $-$ I_a(deuterium)] expected for the trans, cis, and gauche conformations based on plausible trial structures are listed in Table IV. Comparing the isotopic shifts with those experimentally measured shows that the trans form is favored. The trial structure employed bond lengths and angles from PH_3 and PF_3 and a PP bond of 2.22 Å; it was used initially to identify the spectra of both isotopic species.

TABLE IV

CHANGES IN MOMENTS OF INERTIA (AMU Å^2) UPON DEUTERATION PREDICTED FOR SEVERAL CONFORMATIONS BASED ON AN INITIALLY ASSUMED STRUCTURE

	ΔI_a	ΔI_b	ΔI_c
Trans	3.18	9.11	10.37
Gauche	5.72	6.58	8.94
Cis	4.12	6.32	6.63
Obsd	3.21	8.47	9.55

(3) Kraitchman's equations for double substitution[19] in a molecule with C_s symmetry gave hydrogen coordinates of $|a| = 1.928$, $|b| = 1.032$, and $|c| = 0.758$ Å. These were within 1–5% of those predicted by our trial trans structure. If the isomer was cis, the hydrogen a and c coordinates should have been considerably smaller since the hydrogens would be closer to the center of mass. If the hydrogen coordinates were calculated assuming single rather than double deuterium substitution, the coordinates obtained were unreasonably large precluding the possibility that the wrong isotopic species was assigned.

In conclusion the changes in the moments of inertia upon deuteration eliminate the gauche or cis conformation or a structure like that found for H_2NPF_2. They are most consistent with the trans conformation.

Structural Parameters.—There are seven structural parameters for a trans conformation; the data from the two species cannot fix them without one assumption. These structural parameters were calculated for assumed PH bond lengths between 1.38 and 1.44 Å, a range encompassing all known PH bond lengths. The results are included in Table V. It can be seen that some parameters such as d(PP) and d(PF) vary greatly with d(PH). One parameter ∠PPH is particularly insensitive to the value assumed for d(PH).

TABLE V

SETS OF STRUCTURAL PARAMETERS WHICH FIT THE OBSERVED ROTATIONAL CONSTANTS (BOND LENGTHS IN ÅNGSTRÖMS, BOND ANGLES IN DEGREES)

d(PH)	d(PF)	d(PP)	∠HPH	∠HPP	∠FPF	∠FPP
1.380	1.535	2.365	96.8	92.1	103.0	89.9
1.390	1.548	2.325	95.8	91.6	101.4	91.8
1.400	1.558	2.290	94.9	91.2	100.8	93.8
1.410	1.574	2.251	94.1	90.8	99.4	95.6
1.420[a]	1.587	2.218	93.2	90.3	98.2	97.2
1.430	1.604	2.184	92.4	89.9	97.0	98.6
1.440	1.623	2.142	91.6	89.5	95.4	100.2

[a] The structures associated with d(PH) = 1.42 ± 0.01 Å are preferred by the authors. See text.

It seems justified to limit the range of possible structures to those associated with the assumption d(PH) = 1.42 ± 0.01 Å. The reasons are (a) d(PF) is expected to be larger than 1.57 Å based on PF_3 (1.570 Å)[20] and PHF_2 (1.582 Å),[14] (b) ∠FPF is expected to be between 97 and 100° based on PF_3 (97.8°) and HPF_2 (99°), (c) most PP single bond lengths fall in the range 2.22 ± 0.04 Å,[9] and (d) d(PH) is expected to be near 1.42 Å based on PH_3 (1.419 Å)[21] and PHF_2 (1.412 Å). Hence, the structural parameters most consistent with the experimental data and the results from other molecules are $d(\mathrm{PH}) = 1.42 \pm 0.01$ Å, $d(\mathrm{PP}) = 2.18 \mp 0.038$ Å, $d(\mathrm{PF}) = 1.587 \pm 0.013$ Å, $\angle\mathrm{HPH} = 93.2 \mp 1°$, $\angle\mathrm{HPP} = 90.3 \mp 0.4°$, $\angle\mathrm{FPF} = 98.2 \mp 1.2°$, and $\angle\mathrm{FPP} = 97.2 \pm 1.6°$. The uncertainties encompass the range of parameters based on the assumed PH bond length of 1.42 ± 0.01 Å.

Discussion

This section will center upon the two conclusive results of this study, *viz.*, the conformation and the dipole moment. The structural parameters do not warrant a detailed analysis due to their large uncertainties.

It requires several assumptions in order to analyze the total dipole moment of H_2PPF_2 with a bond dipole moment model particularly because of the contributions of the lone pairs. Nevertheless it is interesting to speculate on the size of the PP bond moment by transferring PF and PH bond moments from other molecules and assuming that any lone-pair contributions are contained in those bond moments. Using the bond dipole moments from PF_3[22] and PH_3[23] and the structure discussed above gave μ_a = 0.79 D (observed 1.25 D) and μ_c = 1.32 D (observed 1.16 D). A PP

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bond moment of 0.5 D will nicely raise μ_a and lower μ_c to the observed values only if the negative end is directed to the phosphorus with the fluorine substituents. This value suggests an inductive effect from the fluorines, and the direction of the bond dipole is consistent with the greater Lewis basicity toward borane of the phosphorus with the attached fluorines. It is interesting to note that the same value for the PP bond moment fits both μ_a and μ_c for H_2PPF_2, implying that the bond dipole moments in PF_3, PH_3, and H_2PPF_2 are internally consistent.

This investigation shows that the stable conformation is trans with no evidence for appreciable amounts of a gauche conformer. This is particularly interesting for two reasons. First, there appears to be no tendency for the lone pair on the PH_2 group to form a d_π–p_π bond to the PF_2 end since this would make the PH_2 group planar. This effect can be invoked to rationalize the planar arrangement around the nitrogen in H_2NPF_2[12] and $(CH_3)_2NPF_2$.[11] An analogy to this result has been observed with $N(SiH_3)_3$ which is planar[24] while $P(SiH_3)_3$ is pyramidal.[25]

Second, the stability of the trans form is interesting in view of the electrical asymmetry in H_2PPF_2; apparently an internal attraction between the hydrogens and fluorines is not influential enough to stabilize the gauche isomer. There is, however, some suggestion of an interaction involving the hydrogens since the PPH angle is a "small" 90°. Since H_2PPF_2 readily decomposes to HPF_2, it seems preferable to call the interaction an attraction presumably toward the lone pair on the adjacent phosphorus.

The data now available indicate that all gaseous diphosphines have the trans conformation except H_4P_2. A trans conformation seems readily justified invoking steric repulsion and/or lone pair interactions. These two effects should be the smallest in H_4P_2 so a gauche conformation would be more likely; nevertheless some stabilizing interaction must still operate to give the gauche conformation. The results of this investigation certainly suggest that further studies of the molecular and electronic structure of H_4P_2 and its potential function for rotation about the PP bond are warranted.

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Vibrational Spectra and Assignments for Isotopic Species of Tetraborane(10)[1]

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Four isotopically enriched species of tetraborane(10) have been prepared involving hydrogen, deuterium, boron-10, and boron-11. The infrared spectra of these compounds have been investigated in the gas and solid states in the spectral region from 400 to 4000 cm^{-1}. Low-resolution Raman spectra in the liquid and solid states have been obtained and qualitative polarization measurements made. Vibrational modes of this molecule have been described on the basis of a symmetry analysis and a group vibration approximation. Tentative vibrational assignments have been made for 34 of the 36 fundamentals.

Introduction

Despite the extensive chemical interest in the boron hydrides and the intriguing nature of the hydrogen bridge bond which these compounds contain, spectroscopic attention has been focused almost entirely upon the simplest member of the series, diborane. Experimental difficulties caused by the reactive nature and general thermal instability of the higher hydrides, together with spectroscopic complications inherent in their relatively large size and the lack of isotopic purity of natural boron, seem to have been effective deterrents to study. These compounds clearly deserve considerably more attention than they have been accorded.

In the present work, the vibrational spectra of four isotopic varieties of tetraborane (10), B_4H_{10}, have been investigated in the gas, liquid, and solid states under low resolution in order to arrive at a preliminary set of vibrational assignments. The infrared spectrum of this compound prepared from boron containing the natural isotopic abundance has been reported in the literature, the most detailed results being those of Spielman and Burg,[3] who published the infrared spectrum of the vapor for both the hydrogen and deuterium compounds. Qualitative assignments were given based on frequency shifts and analogies with the spectra of other compounds. No Raman data have been found. A few infrared frequencies for the mixed isotopic species, $B_4H_8D_2$, have also been reported.[4] The only other higher boron hydride which has been given any signifi-

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[1] Based on a dissertation submitted by A. J. Dahl in partial fulfillment of the requirements of the Ph.D. degree to the Horace H. Rackham School of Graduate Studies of The University of Michigan.

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