Advocacy of Negl E_{1j} Extrathermodynamic Assumption. The assumption that there is a negligible liquid junction potential in cells C and D leads to values of $\Delta G_{tr}(M^+)(\text{negl } E_{1j})$ which in most cases are within 1 kcal/g-ion of the corresponding $\Delta G_{tr}(M^+)(\text{TATB})$ values. Considering the relative ease of performing experiments in cells C and D compared with the several steps, including solubilities, involved in applying the

TATB assumption, the potentiometric measurements are to be recommended for semiquantitative estimates of $\Delta G_{tr}(M^+)$.

Microwave Spectrum, Structure, and Dipole Moment of Biphosphine-4

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Abstract: The microwave spectra in the K and R bands of four isotopic species of biphosphine, P_2D_4, $P_2D_3H(C)$, $P_2D_3H(B)$, and P_2H_4, have been measured. The following structural parameters have been determined from a least-squares analysis of the observed moments of inertia: $r(P-D_1) = 1.414 \pm 0.002$ Å, $r(P-D_2) = 1.417 \pm 0.002$ Å, $r(P-P) = 2.2191 \pm 0.0004$ Å, $\angle DPD = 92.0 \pm 0.8°$, $\angle D_1PP = 94.3 \pm 0.2°$, $\angle D_2PP = 99.1 \pm 0.1°$, and ϕ(dihedral) $= 74.0 \pm 2.2°$. The values for the dipole moments obtained from Stark splittings are: P_2D_4, $|\mu_c| = 0.928 \pm 0.005$ D; $P_2D_3H(C)$, $|\mu_a| = 0.02 \pm 0.007$, $|\mu_b| = 0.15 \pm 0.02$ D, $|\mu_c| = 0.91 \pm 0.01$ D, $|\mu| = 0.92 \pm 0.01$ D; $P_2D_3H(B)$, $|\mu_a| = 0.008 \pm 0.007$ D, $|\mu_b| = 0.92 \pm 0.1$ D, $|\mu_c| = 0.04 \pm 0.02$ D, $|\mu| = 0.92 \pm 0.01$ D. The values of the structural parameters are discussed and the conformation is compared with those previously determined for similar molecules.

The symmetry of molecules which have the general formula X_2Y_4 has been the subject of many recent studies.[1-11] The possible structures for the X_2Y_4 type molecules include planar (D_{2h} symmetry), staggered with a twist angle of 90° (D_{2d}), and the three symmetries arising from the nonplanar arrangement of the XY_2 moiety: trans (C_{2h}), gauche (C_2), and cis (C_{2v}). It has been found that for molecules in which the central pair of atoms is a group VA element, N, P, or As, the structures determined have been either trans or gauche. These structures correspond to a pyramidal arrangement of the neighboring atoms and nonbonded electron pairs about the central group VA atoms. The relative amounts of the trans or gauche isomers will depend upon the interactions of the two nonbonded electronic clouds, the steric repulsions of the substituent atoms, the exchange forces electrostatic interactions, and other less important forces.[12] The factors which are ex-

pected to be the most important in determining the conformations of these X_2Y_4 molecules are the X–X bond length and the electronegativity of the Y substituent. Work has shown that an increased X–X bond length favors a greater percentage of the trans isomer.[13] These results can be rationalized on the basis of exchange forces which have a very high power dependence ($1/r^6$) on the X–X bond length, whereas the electrostatic forces are expected to have a relatively small power ($1/r^2$) dependence on this distance. Thus, for long X–X bond lengths, the electrostatic factors are expected to be dominant and, therefore, favor the trans isomers as has been found for these molecules.

The importance of the electronegativity factor can best be demonstrated by considering the isomeric composition of the $P_2(CH_3)_4$ (40% trans) and P_2Cl_4 (95% trans) molecules.[3,4] Since the P–P distance is expected to be nearly the same and the methyl group is about the same size as a chlorine atom, the substituent steric forces should be about the same for these two compounds. However, the electronegativity of the methyl group (~ 2.0) is considerably smaller than that of the chlorine atom (3.0). Thus, it appears that the increased electronegativity of the substituent favors the trans conformer for the phosphines.

Hydrazine has received more attention by spectroscopists than any of the rest of the simple X_2Y_4 molecules of the group VA elements. In the early attempts to assign all of the observed frequencies in the infrared and Raman spectra of hydrazine, various models were

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proposed for this molecule.[13] These included the cis (C_{2v}), the trans (C_{2h}), the gauche (C_2), which could be staggered or semieclipsed, and the tautomeric amine–amide (C_s) models. Although there was some evidence presented at various times for each of these structures, Yamaguchi, et al.,[14] by an analysis of the fine structure of the torsional band centered at 377 cm^{-1}, were able to confirm the structure of N_2H_4 in the gas phase to be gauche with a dihedral angle of approximately 90°. This angle was subsequently confirmed by a microwave study.[15]

Biphosphine has been the most extensively studied of the compounds containing P–P bonds, but there is still considerable uncertainty concerning the molecular symmetry of this molecule. The Raman spectrum of liquid diphosphine was initially interpreted[16] on the basis of the gauche structure, although subsequent work[17] by these same authors showed that the Raman spectrum of the liquid could be satisfactorily interpreted on the basis of the trans conformer. About the same time, Nixon[18] concluded from a study of the infrared spectrum that the gaseous biphosphine molecule has a gauche structure. This conclusion was based mainly on the infrared band contours. In the most recent vibrational study, Frankiss[11] obtained the infrared and Raman spectrum of solid biphosphine and concluded that the molecule has C_{2h} symmetry in the solid. It had been difficult to compare the infrared and Raman spectra in previous investigations, since the spectra were taken in different physical states (infrared of the gas and Raman of the liquid). Thus, it appears that the symmetry of the molecule in the crystalline state should be more certain than that determined for the fluid states.

A recent electron diffraction study of this molecule has been reported by Beagley, et al.,[10] and they obtained the following structural parameters: P–P = 2.218 ± 0.004 Å, P–H = 1.451 ± 0.005 Å, ∠PPH = 95.2 ± 0.6°, and ∠HPH = 91.3 ± 1.4°. The refinement of the dihedral angle converged to 81°, but these authors stated they could not rule out free rotation about the P–P bond. A specimen calculation of molecular intensity for the trans configuration gave a value of $\Sigma W\Delta^2$ insignificantly different from the final value from the refinement which suggests that there is little in the electron diffraction data to establish the preferred configuration as stated by the authors. In order to determine the preferred configuration and structure of gaseous biphosphine, we have undertaken the microwave investigation of P_2D_4, P_2D_3H, and P_2H_4.

Experimental Section

All biphosphine-4 species were prepared by the neutral hydrolysis of commercial calcium phosphide (City Chemical Corp., New York, N. Y.) in a modification of the method of Evers and Street.[19] Instead of attaching the hydrolysis apparatus to a vacuum system, the preparation was done in a flow of nitrogen gas in a manner
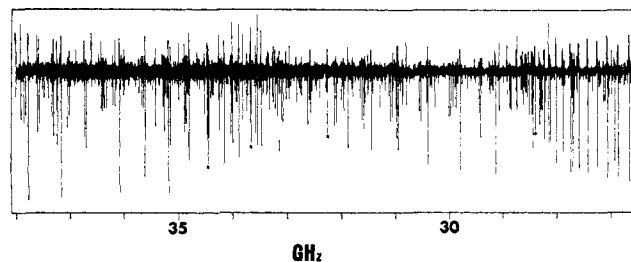
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Figure 1. Microwave spectrum from 26.5 to 38.0 GHz of P_2D_4 and P_2D_3H recorded with a scan speed of 10 MHz/sec. The ordinate scale is in relative absorption with the Stark obes pointing up and the absorption lines pointing down. The 5 ← 5 Q branches of the three species (P_2D_4, $P_2D_3H(C)$, and $P_2D_3H(B)$) are marked with points (•) and the band head for the two P_2D_3H species is labeled with a bar (|).

identical with that used in the preparation of phosphine.[20] Upon conclusion of the reaction, the liquid nitrogen trap in the hydrolysis apparatus was attached to a mercury-free, high-vacuum system equipped with greaseless stopcocks. From this point on, all experimental work was performed in the absence of as much light as was feasible, since biphosphine-4 is light sensitive. The phosphine–biphosphine mixture was transferred to the vacuum system and passed (without pumping) through a trap held at −160° (isopentane slush) into a trap at −196°. This served to remove all traces of PH_3. The material retained in the −160° trap was then subjected to a low-temperature fractionation on a vacuum distillation column.[21] This served to remove any H_2O which had been carried through a −30° bath in the hydrolysis apparatus. The deuterated species P_2D_3H and P_2D_4 were prepared and purified (simultaneously) in a similar manner using commercial D_2O which was known (by ^1H nmr) to be slightly contaminated with H_2O.

Microwave spectra were recorded in the K and R bands using a Hewlett-Packard Model 8460A MRR spectrometer with a Stark cell modulation frequency of 33.3 kHz. All frequencies were measured slightly above Dry Ice temperature ($\sim -60°$), and the accuracy was estimated to be better than ±0.06 MHz. The sample was found to be quite stable at Dry Ice temperatures and no decomposition was noted for periods as long as 10 hr.

Results

The microwave spectrum of P_2D_4 and P_2D_3H for the spectral range 26.5–38.0 GHz is shown in Figure 1. This "compressed" spectrum is characterized by three prominent Q branch series. The lower frequency series, having a band head at $\sim$28583 MHz, is of type C and progresses to lower frequency. This series belongs to the molecule P_2D_4. Each of the Q branch transitions is composed of a doublet separated by $\sim$1.87 MHz. Each line of the doublet has the same Stark effect as is shown in Figure 2. The splitting of the transitions is due to torsional tunneling. The two higher frequency Q branch series are due to the two possible configurations of P_2D_3H. The fact that there are two possible P_2D_3H isomers rules out the possibility of a C_{2v} conformer and leaves as the only possibility the C_2 gauche configuration. The band head for both series is at $\sim$33131 MHz. One of the isomers is predominantly type C and this species will be referred to as $P_2D_3H(C)$, whereas the other isomer is predominantly of type B and will be referred to as $P_2D_3H(B)$. The $P_2D_3H(C)$ series progresses to lower frequency whereas the $P_2D_3H(B)$ series progresses to higher frequency. The assignment and frequencies for the measured lines are listed in Tables I, II, and III. In obtaining the rotational constants for P_2D_4, the average

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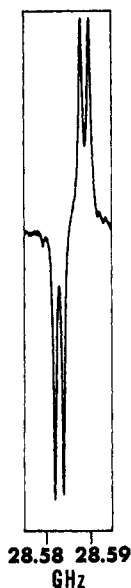(21) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

Figure 2. The $1_{11} \leftarrow 1_{01}$ transition of P_2D_4. The ordinate scale is in relative absorption with the Stark lobes pointing up and the absorption lines pointing down.

Table I. Rotational Transition Frequencies (MHz) of P_2D_4 and P_2H_4

Transition	High	Low	Av	$\nu_{calcd} - \nu_{obsd}$
		P_2D_4		
$1_{11} \leftarrow 1_{01}$	28584.39	28582.54	28583.47	0.30
$2_{12} \leftarrow 2_{02}$	28558.27	28556.39	28557.33	0.24
$3_{13} \leftarrow 3_{03}$	28519.13	28517.28	28518.21	0.20
$4_{14} \leftarrow 4_{04}$	28467.01	28465.17	28466.09	0.13
$5_{15} \leftarrow 5_{05}$	28402.01	28400.13	28401.07	0.07
$6_{16} \leftarrow 6_{06}$	28324.16	28322.27	28323.21	0.02
$1_{10} \leftarrow 0_{00}$	39004.91	39003.06	39003.99	0.50
$6_{06} \leftarrow 5_{14}$	33572.67	33570.75	33571.71	-0.66
$4_{22} \leftarrow 5_{14}$	33622.92	33621.06	33621.99	0.15
$4_{23} \leftarrow 5_{15}$	34013.64	34011.77	34012.71	0.54
		P_2H_4		
$1_{10} \leftarrow 2_{02}$	36661.52	35989.41	36325.47	0.11
$2_{11} \leftarrow 3_{03}$	25031.51	24359.49	24695.35	-0.18
$7_{07} \leftarrow 6_{15}$	22083.11	21408.49	21745.80	0.18
$8_{08} \leftarrow 7_{16}$	33673.23	32997.75	33335.49	-0.11

Table II. Rotational Transition Frequencies (MHz) of $P_2D_3H(C)$

Transition	ν	$\nu_{calcd} - \nu_{obsd}$
$1_{11} \leftarrow 1_{01}$	33133.42	0.40
$2_{12} \leftarrow 2_{02}$	33004.49	0.40
$3_{13} \leftarrow 3_{03}$	32811.66	0.29
$4_{14} \leftarrow 4_{04}$	32555.91	0.15
$5_{15} \leftarrow 5_{05}$	32238.40	0.04
$6_{16} \leftarrow 6_{06}$	31860.50	-0.12
$6_{06} \leftarrow 5_{14}$	29927.23	-0.56
$5_{23} \leftarrow 6_{15}$	34133.64	0.13
$5_{24} \leftarrow 6_{16}$	36835.80	0.42
$6_{25} \leftarrow 7_{17}$	26605.71	-0.20

frequency of the doublets was used. The rotational constants and moments of inertia derived from the frequencies in Tables I, II, and III are listed in Table IV.

Dipole Moment

The dipole moment component of P_2D_4 was calculated from the measured Stark effects of the following

Table III. Rotational Transition Frequencies (MHz) of $P_2D_3H(B)$

Transition	ν	$\nu_{calcd} - \nu_{obsd}$
$1_{10} \leftarrow 1_{01}$	33129.16	0.40
$2_{11} \leftarrow 2_{02}$	33203.52	0.41
$3_{12} \leftarrow 3_{03}$	33315.27	0.36
$4_{13} \leftarrow 4_{04}$	33464.66	0.20
$5_{14} \leftarrow 5_{05}$	33652.17	0.10
$7_{16} \leftarrow 7_{07}$	34143.21	-0.30
$6_{06} \leftarrow 5_{15}$	31548.82	-0.57
$5_{23} \leftarrow 6_{16}$	35968.54	0.04
$5_{24} \leftarrow 6_{15}$	34404.20	0.52

components: $|M| = 1$ of the $1_{11} \leftarrow 1_{01}$ and $|M| = 2$ and 1 of the $2_{02} \leftarrow 2_{12}$ transitions. The dipole moment components of $P_2D_3H(C)$ were calculated from the measured Stark effects of the following components: $|M| = 1$ of the $1_{11} \leftarrow 1_{01}$, $|M| = 2$ and 1 of the $2_{12} \leftarrow 2_{02}$, and $|M| = 3$ and 4 of the $4_{14} \leftarrow 4_{04}$ transitions. The dipole moment components of $P_2D_3H(B)$ were calculated from the measured Stark effects of the following components: $|M| = 1$ of the $1_{10} \leftarrow 1_{01}$, $|M| = 2$ and 1 of the $2_{11} \leftarrow 2_{02}$, and $|M| = 3$ and 2 of the $3_{12} \leftarrow 3_{03}$ transitions. All these components were observed to have a second-order Stark effect. Field strengths were calibrated[22] by using the $3 \leftarrow 2$ transition of OCS at 36488.82 MHz. The stark coefficients were calculated using the method of Golden and Wilson.[23] The calculated and measured Stark coefficients are listed in Table V along with the values of the dipole moment components obtained by a least-squares method.

Structure

The present experimental information (rotational constants and dipole moment components of P_2D_4, $P_2D_3H(C)$, and $P_2D_3H(B)$) allows us to calculate a good least-squares structure for biphosphine. There are seven independent structural parameters for biphosphine: the P–P distance, two P–H distances, the H–P–H angle, two H–P–P angles, and the torsional angle which is measured from the cis conformation. If the approximate structural parameters are taken from the electron diffraction study,[17] the dipole moment components of the two P_2D_3H species can be calculated as a function of the torsional angle. As can be seen from Figure 3, only the torsional angle of $73 \pm 6°$ is consistent with all the observed dipole moment components. More accurate values of all the structural parameters can be obtained by varying the seven structural parameters in a least-squares manner in order to fit the nine observed moments of inertia of the above three isotopic species. The resulting values are listed in Table VI. The $P_2D_3H(C)$ species corresponds to the structure with the H at the near eclipsed position and the $P_2D_3H(B)$ species to the structure with the H at the near trans position. The uncertainties in the calculated values were obtained from the variance–covariance matrix in the usual manner.[24] These values predict the rotational constants and projections of the dipole moment components for P_2D_4, $P_2D_3H(C)$, and $P_2D_3H(B)$ quite accurately. The projection of the dipole moment components is quite sensitive to the

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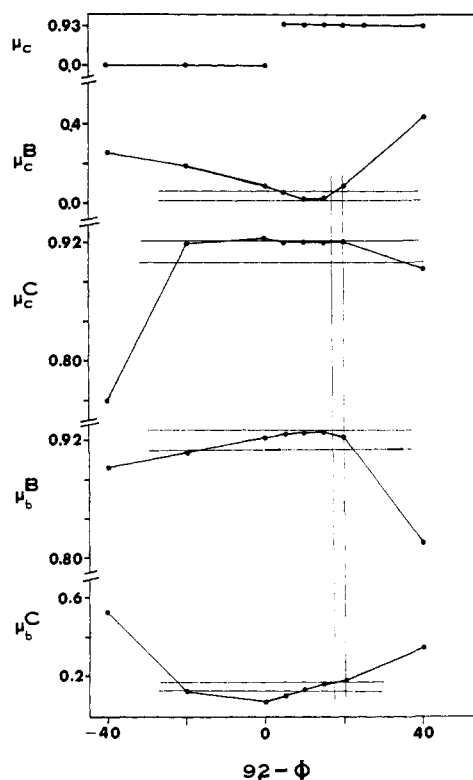(24) H. Kim, *J. Chem. Educ.*, **47**, 120 (1970).

Table IV. The Rotational Constants (MHz) and Moments of Inertia (amu $Å^2$) of Biphosphine

Species	A	B	C	I_a	I_b	I_c
P_2D_4	33793.33 ± 0.19	5210.16 ± 0.05	5184.07 ± 0.04	14.9549	96.9984	97.4865
$P_2D_3H(C)$	38540.95 ± 0.21	5407.92 ± 0.05	5278.60 ± 0.04	13.1127	93.4513	95.7407
$P_2D_3H(B)$	38432.65 ± 0.23	5378.13 ± 0.04	5303.86 ± 0.05	13.1497	93.9689	95.2848
P_2H_4	65433.7 ± 2.8	5831.27 ± 0.74	5815.19 ± 0.30	7.72349	86.6667	86.9063

Table V. Stark Coefficients $((MHz\ cm^2)/V^2)$ and Dipole Moment of P_2D_4, $P_2D_3H(C)$, and $P_2D_3H(B)$

Transition	$|M|$	Obsd $\times 10^5$	Calcd $\times 10^5$
P_2D_4			
$1_{11} \leftarrow 1_{01}$	1	4.182	4.176
$2_{12} \leftarrow 2_{02}$	2	5.012	5.018
$2_{12} \leftarrow 2_{02}$	1	2.921	2.918
$|\mu_a| = 0$			
$|\mu_b| = 0$			
$|\mu_c| = 0.928 \pm 0.005$			
$P_2D_3H(C)$			
$1_{11} \leftarrow 1_{01}$	1	3.288	3.289
$2_{12} \leftarrow 2_{02}$	2	4.488	4.483
$2_{12} \leftarrow 2_{02}$	1	2.663	2.666
$4_{14} \leftarrow 4_{04}$	3	1.864	1.868
$4_{14} \leftarrow 4_{04}$	4	4.939	4.940
$|\mu_a| = 0.02 \pm 0.007$			
$|\mu_b| = 0.15 \pm 0.02$			
$|\mu_c| = 0.91 \pm 0.01$			
$|\mu| = 0.92 \pm 0.01$			
$P_2D_3H(B)$			
$1_{10} \leftarrow 1_{01}$	1	3.624	3.628
$2_{11} \leftarrow 2_{02}$	2	4.291	4.275
$2_{11} \leftarrow 2_{02}$	1	2.261	2.263
$3_{12} \leftarrow 3_{03}$	3	4.660	4.601
$3_{12} \leftarrow 3_{03}$	2	1.315	1.318
$|\mu_a| = 0.008 \pm 0.007$			
$|\mu_b| = 0.92 \pm 0.01$			
$|\mu_c| = 0.04 \pm 0.02$			
$|\mu| = 0.92 \pm 0.01$			

Figure 3. The dipole moment projections as a function of the torsional angle. The actual torsional angle, ϕ, can be expressed as $\phi = 92.71 - \theta$, where 92.71 is the projection of the DPD angle. The horizontal bars represent the error limits of the dipole moment projections and the vertical bars refer to the error limits on the torsional angle from the least-squares fit of the observed moments of inertia. The superscripts C and B refer to $P_2D_3H(C)$ and $P_2D_3H(B)$, respectively. The subscripts b and c refer to the dipole directions.

torsional angle as is shown in Figure 3. As a test of this structure, we calculated the expected rotational constants for P_2H_4. These rotational constants predict only four low J (<9) transitions in the K and R band region. As in the case of P_2D_4, the observed transitions were split into doublets but the spacing was much greater for P_2H_4 ($\sim$673 MHz). The four observed rotational transitions are listed in Table I. The average frequency of the doublets was used to calculate the rotational constants and moments of inertia listed in Table IV. The calculated and observed rotational constants agree quite well for the B and C rotational constants, but are quite far off for the A rotational constant. This discrepancy can be accounted for by a slight lengthening of the P–H bond length as compared to the P–D bond length. The A rotational constant is quite sensitive to the P–H bond length ($\partial A/\partial R_{PH} = -92,400$ MHz/Å) whereas the B and C rotational constants are quite insensitive ($\partial B/\partial R_{PH} = -450$ MHz/Å; $\partial C/\partial R_{PH} = -470$ MHz/Å). If the difference between the observed and calculated A rotational constant (-138.2 MHz) is divided by $\partial A/\partial R_{PH}$, the change in bond length $\Delta R_{PH} = 0.0015$ Å is obtained. Therefore, the P–D bond length is about 0.0015 Å shorter than the P–H bond length. This difference is consistent with other studies of X–H and X–D bond lengths.

Discussion

The two phosphorus–deuterium bond lengths of 1.414 ± 0.002 and 1.417 ± 0.002 Å are within experimental error of being the same length, and the differences may not be significant. However, it should be pointed out that the least-squares fit was vastly improved by allowing these two parameters to vary independently. This bond distance is comparable to the typical P–H bond distance of 1.420 ± 0.005 Å found in phosphine.[25] Beagley, et al.,[10] from their electron diffraction study reported a P–H bond distance of 1.451 ± 0.005 Å, which is considerably longer than one would expect on the basis of previously reported P–H distances.

The moments of inertia were found to be extremely sensitive to the phosphorus–phosphorus bond length. Even if one takes three times the dispersion from the least-squares fit, the uncertainty would still be only 0.001 Å. Our value of r(P–P) of 2.2191 ± 0.0004 Å is

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Table VI. Structural Parameters for Biphosphine

Parameter	Value (microwave)	Value (e.d.)
R_{D1}	1.414 ± 0.002	1.451[a] ± 0.005
R_{D2}	1.417 ± 0.002	
R_{PP}	2.2191 ± 0.0004	2.218 ± 0.004
∠D_1PD_2	92.0 ± 0.8	91.3 ± 1.4
∠D_1PP	94.3 ± 0.2	95.2 ± 0.6
∠D_2PP	99.1 ± 0.1	
φ	74.0 ± 2.2	81 ± 8
P····D_1	2.720	2.76 ± 0.02
P····D_2	2.815	
$D_1···D_2$	2.036	2.08 ± 0.03
$D_1···D_3$	3.058	3.1 ± 0.3
$D_1···D_4$	3.710	3.8[b]
$D_2···D_3$	2.704	2.5[b]

Species	Parameter	Obsd	Calcd
P_2D_4	A	33793.33	33791.80
	B	5210.16	5210.23
	C	5184.07	5184.03
	$\|\mu_a\|$	0	0
	$\|\mu_b\|$	0	0
	$\|\mu_c\|$	0.928	0.928[c]
$P_2D_3H(C)$	A	38540.95	38549.99
	B	5407.92	5407.98
	C	5278.60	5278.55
	$\|\mu_a\|$	0.02	0.02
	$\|\mu_b\|$	0.15	0.18
	$\|\mu_c\|$	0.91	0.91
$P_2D_3H(B)$	A	38432.65	38430.40
	B	5378.13	5378.23
	C	5303.86	5303.78
	$\|\mu_a\|$	0.008	0.001
	$\|\mu_b\|$	0.92	0.92
	$\|\mu_c\|$	0.04	0.07
P_2H_4	A	65433.7	65571.9
	B	5831.27	5830.69
	C	5815.19	5816.63
	$\|\mu_a\|$	0	0
	$\|\mu_b\|$	0	0
	$\|\mu_c\|$		0.928

[a] Possible typographical error 1.415? [b] No error limits reported for these values. [c] A vector of length 0.928 was assumed along the C_2 axis of P_2D_4 and along the pseudo C_2 axes of $P_2D_3H(C)$ and $P_2D_3H(B)$ in order to calculate the projections of the dipole moment components.

within the error limits of the value of 2.218 ± 0.004 Å reported from electron diffraction investigation.[10] This P–P distance is considerably shorter than the value of 2.281 ± 0.003 Å found[26] in the P_2F_4 molecule, but it is similar to the 2.192 ± 0.009 distance found[27] for this parameter in the $P_2(CH_3)_4$ molecule. Because of the relatively large uncertainty in the P–P bond length for the F_2PPH_2 molecule,[28] it does not seem reasonable to compare it with our P–P distance. The inordinately long P–P distance in P_2F_4 is consistent with the electronegativity of the substituent atoms, and these bond distances follow the same trend as those for the N–N bonds in the corresponding hydrazine series.[13]

The DPD angle of 92.0 ± 0.8° is very similar to the corresponding angle in phosphine which was found to have a value of 93.3 ± 0.2°. The two parameters (94.3 ± 0.2° and 99.1 ± 0.1°) associated with the DPP angle are significantly larger than the DPD angle. The two deuteriums which are nearly eclipsed have the

larger DPP angle of 99.1 ± 0.1°. This angle "opening" may indicate repulsion between these deuteriums. In the electron diffraction study, the authors[10] assumed these two angles to be the same and obtained values of 95.6 ± 0.6°.

The most interesting parameter is the dihedral angle. Our data gave a value of 74.0 ± 2.2° for this angle. Beagley, et al.,[10] had reported a value of 81° for this angle which would give a gauche structure with the projection of one of the hydrogens between the two hydrogens on the other phosphorus atom. However, as pointed out in the introduction, these authors[10] stated that they could not distinguish between this model and a freely rotating one from their diffraction data. Thus, it appears that the electron diffraction results are not sensitive to the dihedral angle. It is interesting to note that the parameters obtained from the microwave study reproduce very well all of the observed bonded and nonbonded distances reported from the electron diffraction work with the exception of the P–H bond distance (see Table VI).

There have been three recent[29-31] theoretical calculations on the structure of biphosphine-4. Cowley, et al.,[29] carried out MO calculations on this molecule and concluded that the order of conformational stability is gauche > cis > trans. Robert, et al.,[30] found the conformational stability to be of the order gauche > trans > cis from an ab initio MO calculation. More recently, in another ab initio study, Wagner[31] found the gauche conformer with a dihedral angle of 75° and the trans conformer to be of equal stability with the cis form being of higher energy. It should be pointed out that the structural parameters used by all of these authors are reasonably different from those found in the present study, especially when one considers the two different HPH angles. Also, it might be pointed out that Wagner assumed a P–H distance of 1.437 Å which is considerably longer than the experimental value. However, in all of these calculations, the gauche isomer is predicted to be the most stable conformer. Even though Wagner[31] used slightly incorrect structural parameters, his value for the equilibrium dihedral angle for the gauche conformer is in excellent agreement with the value obtained in the present study. The presence of a small amount of the trans isomer cannot be ruled out from the present study, but a recent vibrational investigation[32] of this molecule showed the presence of only one isomer in the gas phase.

It is clear from our microwave study and the results of the vibrational study[32] that the stable confirmer is the gauche form which can be explained on the basis of the "gauche effect"[33] but is in conflict with current qualitative and phenomenological concepts. On the basis of the "gauche effect," one predicts the most stable structure to be the conformation which has the maximum number of gauche interactions between the adjacent electron and/or polar bonds.[33] Wolfe has further pointed out that, when both electron pairs and adjacent polar bonds are present, there is evidence that

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the observed structure depends not only on the number of gauche interactions but also on the distance between the interacting groups. For these types of molecules, one must consider three types of interactions: (1) electron pair–electron pair, (2) electron pair–polar bond, and (3) polar bond–polar bond. From a comparison of the relative stabilities of the conformers of molecules of the type X_2Y_2 and X_2Y_4, it has been concluded[33] that the electron pair–polar bond interactions are stabilizing for the X_2Y_4 molecules. The experimental dihedral angle in biphosphine is consistent with this stability.

In our observed gauche conformer, the dihedral angle between the nearest symmetry equivalent hydrogens is 18.7° leading to a dihedral angle from the cis conformation of 74.0°. This dihedral angle is very similar in value to the dihedral angles measured for other X_2Y_4 molecules of the group VA elements.[13]

The dipole moment is considerably larger than one would predict from a simple bond moment calculation.[24] The difference is presumably due to effects of the lone pairs. The experimental value of 0.92 D is considerably lower than the calculated value of 3.22 D reported by Cowley, et al.[28]

It was not possible to obtain qualitative or quantitative information on the potential function governing the internal rotation. First, the qualitative nature of the potential function is not known and is likely a mixture of cos θ, cos 2θ, and cos 3θ terms. Secondly, the rotational transitions of the first excited state of the torsion could not be located, presumably because of the very large splitting.

In conclusion, it would appear that further quantitative structural determinations for these X_2Y_4 molecules are warranted, since the "gauche effect"[33] seems adequate to determine the symmetries of molecules whose structures have been determined. However, it should be pointed out that one predicts with this model the electron pair–electron pair interactions in these molecules to be stabilizing which is inconsistent with the usual qualitative concepts currently accepted. Simple MO calculations indicate[34] that molecules of the type $X_2Y_2Z_2$ should be exclusively trans on the basis of the orbital symmetries which was found to be the case for the phosphinodifluorophosphine molecule.[27] Thus, studies of these molecules may not provide as much information on the "gauche effect."

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The Geometry of Intermolecular Aromatic Hydrocarbon–Dialkylaniline Exciplexes

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Abstract: The geometry of intermolecular aromatic hydrocarbon-N,N-dimethylaniline exciplexes was investigated by comparing the singlet quenching rate constants, exciplex energies, and heats of formation of the exciplexes formed upon quenching pyrene excited singlets by N,N-dimethylaniline (1) and 3,5-di-*tert*-butyl-N,N-dimethylaniline (2). The results are in accord with a sandwich-pair geometry for the 1 exciplex and a localized-pair geometry for the 2 exciplex in which the aromatic rings are adjacent but not parallel as in the sandwich-pair case. The dramatic second-order quenching behavior exhibited by 2 also is in accord with the localized-pair geometry. It is shown that about one-half of the exciplex binding energy can be attributed to localized interactions.

Studies of the fluorescence spectra of aromatic hydrocarbon crystals,[1] sandwich dimers,[2,3] and intramolecular excimers[4,5] have shown that a perfectly overlapping sandwich geometry is preferred for excimers which are stabilized by excitation resonance binding. Recent investigations of intramolecular aromatic hydrocarbon–amine exciplexes[6,7] (both anilines and tertiary aliphatic amines) suggest that such specific geometries are not required when charge resonance provides the major stabilizing interaction. It has generally been assumed that the sandwich-pair geometry is preferred for those intermolecular exciplexes in which both partners have π electrons, *i.e.*, aromatic hydrocarbon exciplexes with aromatic amines.[8] This is reasonable if one looks at the nature of the highest occupied molecular orbital of the aniline quencher which acts as the electron donor in these polar exciplexes.

The initial photoelectron spectroscopic data for N,N-dimethylaniline and its derivatives were interpreted as having a π_3, π_2, n molecular orbital ordering[9,10] due to the interaction of the lone-pair n electrons with the

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