JOURNAL OF MOLECULAR SPECTROSCOPY **166**, 210–223 (1994)

Rotational Spectrum, Molecular Constants, Dipole Moment, and Internal Rotation in Vinylphosphine

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The rotational spectra of both $CH_2{=}CHPH_2$ and $CH_2{=}CHPD_2$ have been measured from 8 to 320 GHz. Rotational constants, centrifugal distortion constants, and dipole moment components have been determined. Only the gauche form (dihedral angle of 118.6° between the lone pair of phosphorus and the C=C bond) was found. With assumed bond lengths and bond angles for the vinyl part, the remaining structural parameters have been derived by fitting them to the six rotational constants. Structural results are compared with those of other phosphine derivatives. Internal rotation between two equivalent gauche configurations of $CH_2{=}CHPH_2$ causes splittings of μ_c transitions, which have been analyzed using the phenomenological group-theoretical Hamiltonian. © 1994 Academic Press, Inc.

INTRODUCTION

The unstable compounds ethenylamine $CH_2{=}CHNH_2$ (*1*, *2*), ethenol $CH_2{=}CHOH$ (*3*, *4*), and ethenethiol $CH_2{=}CHSH$ (*5*) have been the subject of many spectroscopic studies. On the other hand, ethenylphosphine (or vinylphosphine) $CH_2{=}CHPH_2$ has only recently been synthesized by flash thermolysis (*6*), and it has been characterized by its photoelectron spectrum (*7*). In the latter studies, the conformation of the most stable rotamer has been determined both experimentally and theoretically. An ab initio calculation using the 4-31G split valence basis set augmented by one set of *d* polarization functions on the P atom indicates that two stable rotamers should exist corresponding to a dihedral angle τ between the lone pair of phosphorus and the C=C bond of 0° and 127°, respectively. For the most stable conformation, the syn form, the P lone pair eclipses the C=C bond ($\tau = 0$). The gauche form ($\tau = 127°$) is 3.5 $kJ \cdot mol^{-1}$ less stable and both forms are separated by low rotation barriers (8.19 and 10.74 $kJ \cdot mol^{-1}$). These results were confirmed by another ab initio calculation at the MP4/6-31G* level (*8*). These predictions indicate that vinylphosphine should have a behavior different from that of the structurally similar molecule vinylamine (*1*, *2*) where only the gauche form has been experimentally found. Although this difference may be explained by a reduction of the lone pair–π interaction in phosphine, it would be interesting to determine experimentally the conformation of the most stable rotamer of vinylphosphine.

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0022-2852/94 $6.00

EXPERIMENTAL DETAILS

Vinylphosphine can be easily prepared according to the procedure described by Cabioch and Denis (*9*). The dimethylvinylphosphonate precursor $CH_2CHP(O)(OCH_3)_2$ was selectively reduced by dichloroalane $AlHCl_2$, prepared according to Ashby's method (*10*). The reduction was carried out in tetraglyme at 0°C in a continuously evacuated flask. The dimethylvinylphosphonate was slowly added to the reducing mixture. Vinylphosphine, which distilled as soon as it was formed, passed through a trap cooled to −100°C to remove most of the impurities and was then condensed into a liquid nitrogen cold trap, with *n*-dibutylether as solvent. The mixture was finally collected in a Schlenk flask and stored at −15°C. The P-dideuterated compound was obtained using lithium and aluminium deuteride $LiAlD_4$. We didn't attempt removing the small amount of P-monodeuterated vinylphosphine which was also obtained. Vinylphosphine in dibutylether can be kept for several months. Moreover, the solvent can be easily removed before the introduction of vinylphosphine in the microwave cell, by inserting a trap at −100°C between the Schlenk flask containing the mixture and the absorption cell. The stability of the sample in the closed brass cell was more than 30 mn at room temperature.

The spectrum in the range 8–100 GHz was observed using a computer-controlled Stark-modulation spectrometer (*11*). The millimeter-wave spectrum in the range 100–320 GHz was measured with a computer-controlled millimeter-wave spectrometer using superheterodyne detection (*12*). The accuracy of the frequency measurements is about 50 kHz for both spectrometers.

AB INITIO CALCULATIONS

Before starting to record the rotational spectrum, we made a new set of ab initio calculations for vinylphosphine in order to obtain additional information on the struc-

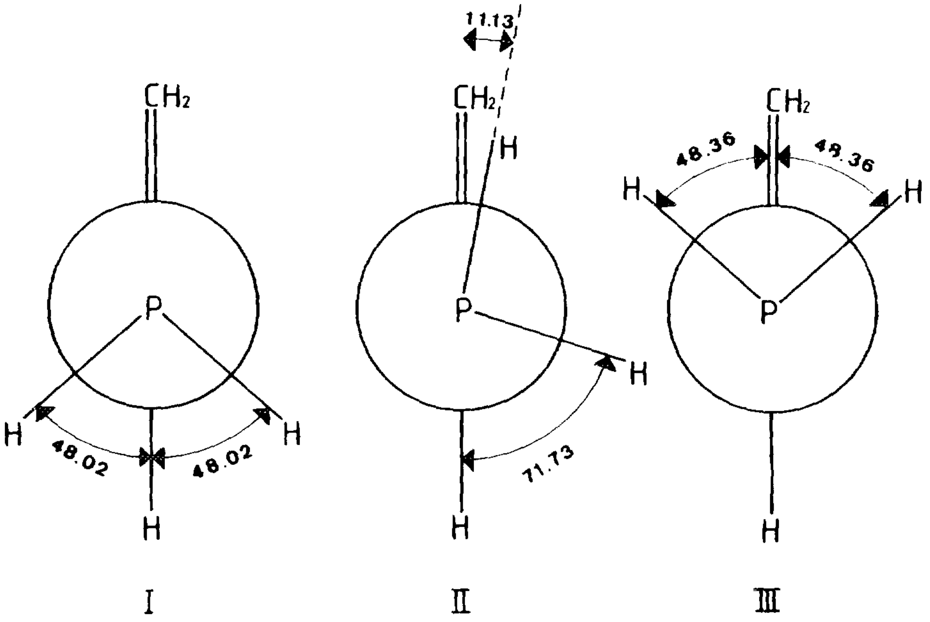

FIG. 1. The three rotamers of vinylphosphine, according to ab initio calculations: the syn form (I), the gauche form (II), and the anti form (III). Bond angles are given in degrees.

ture, rotational constants, and electric dipole moment of the possible stable rotamers. Computations have been carried out using standard STO 3-21G* and 6-31G* orbitals and the Gaussian 82 program (*13*). In these calculations we have found three stable rotamers (see Fig. 1), the syn form (I), the gauche form (II), and the anti form (III). In the first series of calculations we have used the 3-21G* basis set and the predicted bond angles and distances have been used as input for the 6-31G* computations. The results obtained using both basis sets are similar and here we only report those for the 6-31G* orbitals. Full geometry optimization has been used except for the restriction

TABLE I

Results of ab Initio Calculations of Vinylphosphine Using Standard STO 6-31G* Orbitals

	I	IIa	IIb	III
Rotamer	Syn	Gauche		Anti
C_1=C_2	1.3211	1.3200	1.3200	1.3200
C_2-P	1.8324	1.8330	1.8317	1.8460
C_1-H_1	1.0764	1.0763	1.0763	1.0765
C_1-H_2	1.0768	1.0764	1.0764	1.0771
C_2-H_3	1.0778	1.0788	1.0788	1.0776
P-H_4	1.4046	1.4046	1.4046	1.4032
P-H_5	1.4046	1.4021	1.4021	1.4032
$\angle C_1C_2P$	121.42	126.46	126.21	126.46
$\angle H_1C_1C_2$	121.99	122.41	122.43	122.38
$\angle H_2C_1C_2$	121.56	121.39	121.39	121.46
$\angle H_3C_2C_1$	119.33	118.96	118.92	118.76
$\angle H_4P C_2$	98.75	98.34	98.95	99.26
$\angle H_5PC_2$	98.75	98.42	98.48	99.26
$\angle H_4P C_2H_3$	48.02	71.73	73.82	-131.64
$\angle H_5P C_2C_1$	131.98	-11.13	-13.78	-48.36
$\angle P C_2C_1H_1$	0	0	4.48	0
$\angle H_2C_1C_2P$	180	180	184.83	180
$\angle H_3C_2C_1H_2$	0	0	-0.24	0
E / Hartree	-419.3277223	-419.3256029	-419.32558633	-419.3229219
ΔE /kJ.mol^{-1}	0	5.564	4.881	12.603
A /MHz	41382	41502	41489	40463
B /MHz	5483	5430	5440	5393
C /MHz	5049	4965	4971	4961
Δ /m$_u$ Å^2	-4.2897	-3.4606	-3.4161	-4.3297
μ_a /D	0.843	0.962	0.936	1.316
μ_b /D	0.874	0.146	0.136	0.633
μ_c /D	0	0.688	0.639	0

Bond lengths in Å and bond angles in degrees.
Conversion factors : 1 hartree = 2625.501047 kJ.mol^{-1}; 1 m$_u$.Å^2 = 505379.1 MHz.
$\Delta = I_c - I_a - I_b$, is the inertial defect.

of C_s symmetry for the syn (I) and anti (III) rotamers. For the gauche form the constraint of vinyl group planarity has been imposed in the first step (IIa), and in the subsequent calculation total relaxation has been allowed (IIb). The results obtained for the 6-31G* basis set are shown in Table I. The atom numbering scheme used in Table I is shown in Fig. 2. The syn form (I) is predicted to be 4.88 $\mathrm{kJ \cdot mol^{-1}}$ more stable than the gauche form and 12.60 $\mathrm{kJ \cdot mol^{-1}}$ more stable than the anti form. It can also be observed that for the gauche form a small tilt of the P atom is predicted with respect to the vinyl group plane. Due to the predicted stability differences only the syn and gauche rotamers have been considered in the microwave spectrum analysis.

ANALYSIS OF THE GROUND STATE SPECTRUM

According to the ab initio structure, the rotational spectrum of both the syn and gauche rotamers should be characteristic of a prolate top with strong μ_a transitions. A spectrum was first predicted for both rotamers using the ab initio rotational constants calculated in the preceding section. The three low-J $2 \leftarrow 1$ $^aR_{0,1}$ transitions were easily found and assigned by their Stark effect. Then higher-J μ_a transitions were assigned by the "bootstrap" method as described by Kirchhoff (*14*). Accurate values of the B and C rotational constants as well as some centrifugal distortion constants were calculated from a fit to the spectrum. To determine the A rotational constant, we tried to assign μ_b transitions, but without success. Furthermore the values of the B and C rotational constants do not allow us to determine which rotamer was found, because both rotamers have similar B and C constants. So we decided to determine the components of the dipole moment (see next section). It appeared that the μ_b component is nearly zero, which explains our failure to observe μ_b transitions. On the other hand, the μ_c component is large enough to permit the observation of μ_c transitions. After some searching, they could indeed be assigned. They were found split, and this splitting can be explained by the internal rotation of the $-PH_2$ group and will be analyzed in a subsequent section. To determine the rotational and centrifugal distortion constants, the mean frequency of the split transitions was used. The rotational spectrum of $CH_2{=}CHPD_2$ was analyzed in the same way but no splitting was observed. The measured frequencies are given in Tables II and III for $CH_2{=}CHPH_2$ and in Table IV for $CH_2{=}CHPD_2$. In order to derive the rotational and centrifugal distortion constants a least-squares program based on the Hamiltonian of Watson (*15*) was used. The Hamiltonian matrix was set up in the I^r representation of the A reduction and was directly diagonalized. The derived parameters are listed in Table V, together with their standard deviations and their correlation coefficients.

DIPOLE MOMENT

The Stark lobes of three different ^aR transitions of the ground vibrational state of vinylphosphine were precisely measured using a dc electric field in the absorption cell

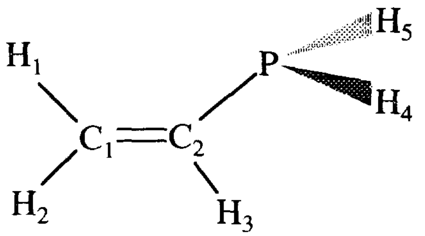

FIG. 2. The atom numbering in vinylphosphine.

TABLE II

Unsplit Transition Frequencies (MHz) in Vinylphosphine

J	K_a	K_c ←	J	K_a	K_c	Exp.	e.-c.[a]	J	K_a	K_c ←	J	K_a	K_c	Exp.	e.-c.[a]
2	0	2	1	0	1	20859.473	0.000	19	6	13	18	6	12	198346.011	-0.021
2	1	2	1	1	1	20380.641	0.019	19	7	12	18	7	11	198313.871	-0.008
2	1	1	1	1	0	21348.430	-0.047	19	9	10	18	9	9	198295.830	0.339
3	0	3	2	0	2	31276.543	-0.050	19	11	9	18	11	8	198307.670	0.027
3	1	3	2	1	2	30567.799	0.109	19	12	8	18	12	7	198320.307	-0.136
3	1	2	2	1	1	32019.388	-0.004	19	13	7	18	13	6	198336.600	0.028
4	0	4	3	0	3	41678.622	0.025	19	14	6	18	14	5	198355.578	0.056
4	1	3	3	1	2	42686.409	0.133	19	15	5	18	15	4	198377.164	0.230
4	2	2	3	2	1	41774.756	-0.272	20	0	20	19	0	19	203639.456	-0.014
5	0	5	4	0	4	52060.465	-0.054	20	1	20	19	1	19	202464.943	-0.093
5	1	5	4	1	4	50929.077	-0.003	20	2	19	19	2	18	207497.730	0.185
5	1	4	4	1	3	53347.750	0.039	23	0	23	22	0	22	233303.536	-0.023
14	1	13	13	1	12	148776.727	-0.060	23	2	22	22	2	21	238206.765	-0.038
14	2	12	13	2	11	147727.341	-0.048	23	6	17	22	6	16	240150.216	-0.046
14	2	13	13	2	12	145663.080	0.006	23	7	16	22	7	15	240086.853	0.324
15	0	15	14	0	14	153965.614	0.122	23	8	15	22	8	14	240053.292	0.241
15	1	15	14	1	14	152229.231	-0.055	23	10	13	22	10	12	240034.204	-0.013
15	1	14	14	1	13	159283.652	-0.119	23	12	11	22	12	10	240050.335	-0.038
15	2	14	14	2	13	156003.426	-0.038	30	1	29	29	1	28	312203.628	0.047
15	2	13	14	2	12	158478.782	-0.060	30	2	28	29	2	27	318740.995	0.175
15	3	13	14	3	12	156720.612	-0.043	30	3	27	29	3	26	317590.981	-0.005
15	3	12	14	3	11	156914.493	-0.022	30	4	26	29	4	25	314571.547	0.026
15	4	12	14	4	11	156654.238	0.479	30	4	27	29	4	26	313921.797	0.138
15	4	11	14	4	10	156658.587	-0.570	30	5	25	29	5	24	313679.381	0.002
15	5	10	14	5	9	156592.706	-0.051	30	5	26	29	5	25	313638.513	-0.004
15	6	9	14	6	8	156564.007	-0.013	30	6	24	29	6	23	313376.005	-0.312
15	7	8	14	7	7	156551.559	-0.150	30	6	25	29	6	24	313375.160	0.346
15	8	7	14	8	6	156548.599	0.034	30	7	24	29	7	23	313220.404	0.134
15	10	5	14	10	4	156557.962	-0.031	30	8	23	29	8	22	313130.842	-0.053
15	11	4	14	11	3	156567.842	-0.007	30	9	22	29	9	21	313079.915	-0.033
19	1	18	18	1	17	200996.527	-0.057	30	10	21	29	10	20	313053.383	-0.108
19	2	18	18	2	17	197228.238	-0.346	30	11	20	29	11	19	313043.632	-0.149
19	2	17	18	2	16	201596.948	-0.078	30	12	19	29	12	18	313046.184	-0.024
19	4	16	18	4	15	198531.732	0.075	30	13	18	29	13	17	313057.741	-0.129
19	4	15	18	4	14	198560.090	-0.146	30	14	17	29	14	16	313076.798	-0.057
19	5	15	18	5	14	198410.363	0.105	31	0	31	30	0	30	312440.275	-0.020
19	5	14	18	5	13	198410.733	-0.192	31	2	30	30	2	29	319351.213	0.015

a) Calculated with the parameters of Table IX.

with a small square wave superposed. Each component was studied for about five different voltages. The measured Stark lobes were chosen so that they had a great dependence on both μ_b and μ_c. The cell was calibrated with the $J = 3 \leftarrow 2$ transition of OCS [$\mu = 0.71529$ D] (*16*). The observed Stark shifts were found to be proportional to the square of the applied field, and the second-order perturbation theory treatment has been used. We did not fix any of the dipole moment components. μ_b was found to be extremely small, while μ_a and μ_c have the same order of magnitude. The results are listed in Table VI.

As can be seen from Table I there are large differences between the ab initio values and the experimental values. This result is not very surprising. In fact it is well established that it is difficult to calculate accurate ab initio values for the dipole moment. The total dipole moment of $CH_2{=}CHPH_2$, $\mu = 0.835$ D, is a little bit smaller than

TABLE III

Split Transition Frequencies (MHz) in Vinylphosphine

						Symmetry A		Symmetry B	
J	K_a	K_c ←	J	K_a	K_c	Exp.	e.-c.a)	Exp.	e.-c.a)
1	1	1	1	0	1	35016.603	-0.147	35034.676	0.087
2	1	2	2	0	2	34537.784	-0.116	34555.833	0.094
3	1	3	3	0	3	33828.912	-0.087	33846.907	0.072
4	1	4	4	0	4	32901.274	-0.043	32919.210	0.065
5	1	5	5	0	5	31769.877	-0.009	31787.720	0.021
6	1	6	6	0	6	30453.473	0.036	30471.222	-0.001
7	1	7	7	0	7	28974.321	0.072	28991.947	-0.044
8	1	8	8	0	8	27357.971	0.114	27375.430	-0.105
7	0	7	6	1	5	32132.625	-0.243	32115.326	0.206
3	1	2	2	0	2	68009.012	-0.071	68026.972	0.051
19	2	18	19	1	18	63707.488	-0.016	63708.632	-0.492
20	2	19	20	1	19	59873.752	-0.019	59875.552	-0.033
21	2	20	21	1	20	56001.320	-0.034	56003.536	0.131
22	2	21	22	1	21	52118.916	-0.102	52121.508	0.153
23	2	22	23	1	22	48256.701	-0.123	48259.605	0.102
24	2	23	24	1	23	44445.606	0.136	44448.927	0.375
25	2	24	25	1	24	40715.250	-0.222	40719.045	0.022
26	2	25	26	1	25	37096.216	-0.019	37100.421	0.092
27	2	26	27	1	26	33615.119	0.041	33619.739	-0.051
28	2	27	28	1	27	30296.432	0.151	30301.453	-0.235
17	1	17	16	2	15	32734.369	-0.360	32733.588	-0.020
18	1	18	17	2	16	38493.456	-0.529	38492.768	-0.065
20	1	20	19	2	18	49226.754	0.634	49225.026	0.122
21	1	21	20	2	19	54209.004	0.188	54207.592	0.023
22	1	22	21	2	20	58944.208	0.029	58942.888	-0.014
24	1	24	23	2	22	67703.392	-0.058	67702.144	0.025
25	1	25	24	2	23	71744.700	-0.118	71743.476	0.011
19	3	17	18	3	16	198575.745	0.031	198575.456	-0.079
19	3	16	18	3	15	199191.356	0.045	199191.008	-0.262
22	2	20	21	2	19	233879.698	-0.495	233879.444	0.092
30	3	28	29	3	27	313149.403	-0.181	313148.973	0.219

a) Calculated with the parameters of Table IX.

the value found for $CH_2{=}CHNH_2$, $\mu = 1.144$ D (*1*). This result parallels that found for CH_3PH_2 where the dipole moment $\mu = 1.10$ D (*17*) is also a little bit smaller than that of CH_3NH_2, $\mu = 1.283$ D (*18*). It is in agreement with the fact that P is less electronegative than N.

STRUCTURE

Both the inertial defect and the components of the electric dipole moment show that the observed form is the gauche one. The predicted 6-31G* B and C rotational constants for this rotamer have a reasonable agreement with those obtained experimentally. However, the differences between the observed and the predicted A rotational constant is about 1 GHz. In order to obtain a structure in agreement with the observed rotational constants we have tried to fit some structural parameters to the six available rotational constants.

In a first series of fits we have assumed a reasonable structure for the vinyl group, taking into account the bond distances and angles reported for ethylene (*19*) and

TABLE IV

Transition Frequencies (MHz) in Vinylphosphine-d_2

J	K_a	K_c ←	J	K_a	K_c	Exp.	e.-c.	J	K_a	K_c ←	J	K_a	K_c	Exp.	e.-c.
3	0	3	2	0	2	29877.945	0.001	15	3	12	14	3	11	150090.652	-0.015
3	1	3	2	1	2	29199.494	0.020	15	3	13	14	3	12	149784.553	-0.040
3	1	2	2	1	1	30598.215	0.008	15	4	11	14	4	10	149736.492	-0.002
4	1	4	3	1	3	38925.282	-0.006	15	4	12	14	4	11	149725.403	0.004
5	0	5	4	0	4	49713.712	0.036	15	6	9	14	6	8	149602.502	-0.062
5	1	4	4	1	3	50975.000	0.021	15	7	8	14	7	7	149578.612	-0.023
5	2	4	4	2	3	49823.560	0.070	15	8	7	14	8	6	149564.770	-0.011
5	2	3	4	2	2	49946.784	0.000	15	9	6	14	9	5	149556.898	0.059
6	0	6	5	0	5	59588.584	0.008	16	1	16	15	1	15	154878.767	-0.006
6	1	6	5	1	5	58357.108	-0.040	20	0	20	19	0	19	193882.347	0.038
6	1	5	5	1	4	61151.404	-0.012	20	2	19	19	2	18	197966.282	-0.006
6	2	5	5	2	4	59776.160	-0.008	20	2	18	19	2	17	203273.277	0.034
6	2	4	5	2	3	59991.276	-0.010	20	3	18	19	3	17	199748.015	0.051
6	3	4	5	3	3	59837.124	0.090	20	4	17	19	4	16	199807.878	0.018
6	3	3	5	3	2	59839.804	-0.099	20	4	16	19	4	15	199891.232	-0.014
7	0	7	6	0	6	69427.432	-0.083	20	6	14	19	6	13	199536.406	-0.064
7	1	7	6	1	6	68060.656	0.030	20	7	14	19	7	13	199476.532	-0.048
7	2	6	6	2	5	69722.356	0.057	20	8	13	19	8	12	199440.237	-0.014
7	2	5	6	2	4	70064.852	0.032	20	9	12	19	9	11	199417.593	0.057
15	0	15	14	0	14	146587.388	0.014	21	0	21	20	0	20	203325.668	-0.059
15	1	14	14	1	13	151960.404	-0.002	21	1	21	20	1	20	202702.197	0.044
15	2	14	14	2	13	148929.449	0.003								

several vinyl derivatives (*2, 4, 20*). A value of 1.325 Å has been chosen for the C=C distance, of the same order as those reported for vinylalcohol (*4, 20*) and vinylamine (*2*). This separation is smaller than those reported for ethylene (1.339 Å) (*19*) and the halogenated vinyl derivatives (~1.330 Å) (*20*). For the CH distances and CCH

TABLE V

Molecular Constants for Vinylphosphine

CH_2=$CHPH_2$										
A (MHz)	40484.147 (16)	1.000								
B (MHz)	5458.08209 (47)	0.103	1.000							
C (MHz)	4974.18534 (44)	-0.105	0.270	1.000						
Δ_J (kHz)	2.79928 (44)	-0.084	0.476	0.387	1.000					
Δ_{JK} (kHz)	-23.949 (12)	0.021	0.285	0.273	-0.151	1.000				
Δ_K (kHz)	435.2 (3.8)	0.874	-0.024	-0.304	-0.102	-0.177	1.000			
δ_J (kHz)	0.39464 (22)	0.032	0.594	-0.493	0.207	-0.118	-0.004	1.000		
δ_K (kHz)	-9.997 (88)	0.006	0.055	-0.015	0.773	-0.217	0.106	0.083	1.000	
Φ_{KJ} (Hz)	-3.123 (67)	0.002	0.217	0.193	-0.056	0.937	-0.163	-0.099	-0.052	1.000
CH_2=$CHPD_2$										
A (MHz)	31366.998 (51)	1.000								
B (MHz)	5216.9275 (30)	0.262	1.000							
C (MHz)	4750.7178 (27)	-0.339	-0.860	1.000						
Δ_J (kHz)	2.5062 (23)	-0.240	0.473	-0.273	1.000					
Δ_{JK} (kHz)	-7.297 (15)	0.071	-0.217	0.306	-0.698	1.000				
δ_J (kHz)	0.3337 (18)	-0.008	0.884	-0.829	0.371	-0.224	1.000			
δ_K (kHz)	-18.94 (46)	-0.272	0.329	-0.356	0.872	-0.738	0.273	1.000		

The uncertainties shown in parentheses are in units of the last digits and are standard errors.

TABLE VI

Observed and Calculated Stark Coefficients and Derived Components of the Electric Dipole Moment for the Ground Vibrational State of Vinylphosphine

$J\ (K_a, K_c)$	←	$J\ (K_a, K_c)$	$\lvert M \rvert$	$\Delta\nu / E^2$ ($Hz.V^{-2}.cm^2$) exp.	calc.
3 (0, 3)		2 (0, 2)	0	-1.0795	-1.0604
3 (0, 3)		2 (0, 2)	1	-0.7670	-0.7483
3 (0, 3)		2 (0, 2)	2	0.1892	0.1881
3 (1, 3)		2 (1, 2)	1	1.8760	1.8713
3 (1, 3)		2 (1, 2)	2	7.6620	7.6426
3 (1, 2)		2 (1, 1)	0	-2.4200	-2.4248
3 (1, 2)		2 (1, 1)	1	-3.9450	-3.9322
3 (1, 2)		2 (1, 1)	2	-8.4765	-8.5036
$\mu_a^2 = 0.4434(10)$ D				$\lvert\mu_a\rvert = 0.6659(7)$ D	
$\mu_b^2 = -0.0022(18)$ D				$\lvert\mu_b\rvert = 0$ D	
$\mu_c^2 = 0.2536(16)$ D				$\lvert\mu_c\rvert = 0.5036(16)$ D	
				$\lvert\mu_T\rvert = 0.8349(9)$ D	

The uncertainties shown in parentheses are in units of the last digit and are standard errors.

angles we have assumed the values reported for ethylene (*19*) of 1.087 Å and 121.3°, respectively. Concerning the PH_2 group we have assumed that the P atom lies in the vinyl plane with a value of 1.414 Å for the PH bond length, in agreement with the reported values for different phosphines (*21–24*). On the basis of these assumed parameters, we have fitted the P–C bond length, the CCP, HPC, and HPH angles, and the dihedral angle between the bisector of the HPH angle and the vinyl plane. The results are collected in Table VII (column a).

In a second series of calculations we have used the ab initio bond lengths and angles (column IIa of Table I) as the starting point to fit the structure. Using the same procedure as before we have fixed the ab initio vinyl group structure and PH distances and fitted the same parameters. The results are collected on Table VII (column b). It can be observed that the main differences between both structures come from the dihedral angles which define the orientation of the PH_2 group with respect to the vinyl plane. The dihedral angle τ between the lone pair of phosphorous and the C=C bond (see Fig. 3) take values of 111° for structure (a) and 118.6° for structure (b). These values are smaller than that predicted from ab initio calculations of 120.3°. In both series of fits the structural parameters for the PH_2 group give reasonable values in comparison with those reported for other phosphines (*21–24*).

INTERNAL ROTATION

It has been shown that the structure of vinylphosphine is that of a gauche form. There are two equivalent gauche conformations (Fig. 3). The splittings of μ_c transitions show that a tunneling between both gauche configurations is possible. Since the symmetry of the internal rotor ($-PH_2$ group) is low, it would be impossible to calculate a reliable potential function for internal rotation from the observed splittings in the ground vibrational state. We have decided to derive and apply a phenomenological group-theoretical Hamiltonian which is based on a formalism for slow tunneling be-

TABLE VII

Results of the Fit of Some Structural Parameters (Bond Lengths in Å and Angles in Degrees) of Vinylphosphine to the Rotational Constants of $CH_2{=}CHPH_2$ and $CH_2{=}CHPD_2$

	(a)	(b)	
C=C	1.325[a]	1.320[b]	
C-H	1.087[a]	1.076[b]	
P-H	1.414[a]	1.404[b]	
C-P	1.837	1.845	
$\angle$ CCH	121.3[a]	122.4[b]	
$\angle$ CPH	97.0	98.7	
$\angle$ CCP	125.1	124.7	
$\angle$ HPH	92.4	94.1	
$\angle H_5PCC$	-21.5	-13.67	
$\angle H_4PCH_3$	63.5	70.83	
	Calc.	Calc.	Exp.
$CH_2{=}CHPH_2$			
A /MHz	40487	40487	40484.147
B /MHz	5459	5456	5458.082
C /MHz	4976	4973	4974.185
Δ /m_u Å^2	-3.496	-3.486	-3.476
$CH_2{=}CHPD_2$			
A /MHz	31367	31369	31366.998
B /MHz	5218	5215	5216.928
C /MHz	4751	4749	4750.718
Δ /m_u Å^2	-6.592	-6.602	-6.605

Note. Results assume (i) a reasonable structure for the vinyl group and PH distance (see text), and (ii) ab initio structure IIa for the vinyl group and PH distance.

[a] Assumed values.

[b] Ab initio values. See Table I, conformer IIa.

tween equivalent frameworks described by Dalton (*25*). The detailed analysis of the formalism applied for internal rotation in H_2O_2 has been given by Hougen (*26*). In Fig. 3 the two nonsuperimposable equilibrium frameworks of vinylphosphine are shown. The second framework can be obtained from the first one by application of a permutation-inversion (PI) operation (45)*, where (45) means a permutation of the coordinates of hydrogen atoms 4 and 5 and the asterisk means an inversion of all coordinates in the center of mass of the molecule. When the torsional angle τ is measured from the double bond of the vinyl group to the electron pair on the phosphine group in the direction given by the positions of atoms H_4 and H_5, then the (45)* operation changes the sign of the torsional coordinate ($\tau \rightarrow -\tau$). The molecular axis system (x, y, z) is so defined that the z axis is located along the C–P bond and the y

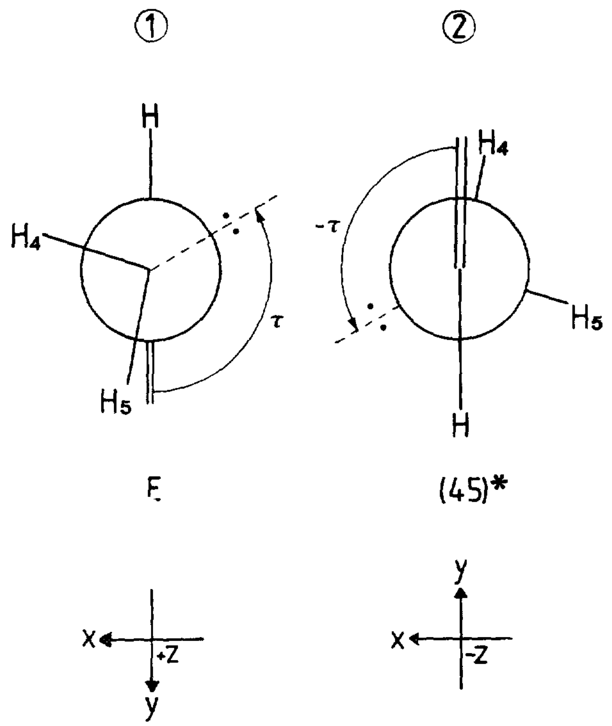

FIG. 3. The two nonsuperimposable equilibrium configurations of vinylphosphine. The second framework can be generated from the first one by the PI operation (45)*. This operation is equivalent to the rotation by π about the x axis of the molecular axis system.

axis lies in the plane of vinyl group, the double bond showing the positive direction of the y axis. The x axis is chosen to form a right-handed axis system. Thus, the PI operation (45)* is equivalent to the rotation about the x axis by π. With each equilibrium configuration a localized torsional function can be associated. In framework 1 the torsional function ψ_1 is localized at the minimum $\tau_e = \tau_0$, and in framework 2 $\tau_e = -\tau_0$. Using these functions, a torsional tunneling matrix H can be generated which is shown in Fig. 4. After diagonalization, the torsional eigenvalues $G(A)$ and $G(B)$ are obtained, of symmetry A and B, respectively. It should be noted that the off-diagonal tunneling matrix element T is added to the torsional energy E_v for the A species and subtracted for the B species. Any single equilibrium configuration of vinylphosphine has no symmetry operations. When the effects of Coriolis interaction are neglected, it is well known that one can use the asymmetric rotor Hamiltonian to divide the rotational levels into one of the four types K_aK_c = ee, eo, oe, oo. If the internal rotation tunneling is possible, each of these levels splits into two components which will be labeled A or B. In general, the Coriolis-type perturbations ($\Delta K = \pm 1$) can mix levels with different parities of K_aK_c. In many cases it is possible to neglect these $\Delta K = \pm 1$ perturbations (*26*). Then the rotational energy levels can still be labeled by the quantum numbers J, K_aK_c appropriate for the asymmetric rotor and a symmetry label A or B defining the tunneling component. The functions symmetrical and antisymmetrical under the PI symmetry operation (45)* are labeled A and B, respectively. We adopt a phenomenological rotational Hamiltonian,

$$\begin{array}{c|cc} & 1 & 2 \\ \hline 1 & E_v & T \\ 2 & T & E_v \end{array} \qquad \begin{aligned} E_v &= \langle \psi_1 | \hat{H} | \psi_1 \rangle = \langle \psi_2 | \hat{H} | \psi_2 \rangle \\ T &= \langle \psi_1 | \hat{H} | \psi_2 \rangle = \langle \psi_2 | \hat{H} | \psi_1 \rangle \end{aligned}$$

$$\begin{aligned} G(A) &= E_v + T \qquad & |A\rangle_t &= (\psi_1 + \psi_2)/\sqrt{2} \\ G(B) &= E_v - T \qquad & |B\rangle_t &= (\psi_1 - \psi_2)/\sqrt{2} \end{aligned}$$

FIG. 4. The Hamiltonian matrix H_t for the internal rotation tunneling problem in vinylphosphine. The diagonal elements E_v represent the one-framework torsional energy, and the off-diagonal elements T arise from the tunneling between frameworks. The torsional eigenvalues $G(A)$ and $G(B)$, and eigenfunctions $|A\rangle_t$ and $|B\rangle_t$, are of the species A and B, respectively.

$$\begin{aligned} \hat{H} = {} & h_v + h_j\hat{J}^2 + h_k\hat{J}_z^2 + h_{jj}\hat{J}^4 + h_{jk}\hat{J}^2\hat{J}_z^2 + h_{kk}\hat{J}_z^4 + h_{jjj}\hat{J}^6 + h_{jjk}\hat{J}^4\hat{J}_z^2 + h_{jkk}\hat{J}^2\hat{J}_z^4 \\ & + h_{kkk}\hat{J}_z^6 + f(\hat{J}_+^2 + \hat{J}_-^2) + f_j\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) + \tfrac{1}{2} f_k[\hat{J}_z^2(\hat{J}_+^2 + \hat{J}_-^2) + (\hat{J}_+^2 + \hat{J}_-^2)\hat{J}_z^2] \\ & + \mathrm{d}(\hat{J}_+^4 + \hat{J}_-^4) + (q + q_j\hat{J}^2 + q_k\hat{J}_z^2)\hat{J}_z + g(\hat{J}_+^2 - \hat{J}_-^2) + p(\hat{J}_+^4 - \hat{J}_-^4), \end{aligned} \tag{1}$$

where all parameters are functions of the torsional coordinate τ, and $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ are ladder operators of angular momentum. Since the (45)* operation is equivalent to the rotation by π about the x axis, the angular momentum operators $\hat{J}_y$ and $\hat{J}_z$ transform according to the B species, whereas the $\hat{J}_x$ operator according to the A species. Since the Hamiltonian in Eq. (1) must be of species A, the parameters h, f, and d transform as the even functions of τ (i.e., as the A species) and the parameters q, g, and p as the odd functions of τ (i.e., as the B species). The PI symmetry operation (45)* changes the sign of τ and in the picture of slow tunneling generates the second framework from the first one (and vice versa). Thus, the parameters q, g, and p in the phenomenological Hamiltonian will generate the splittings of the rotational levels.

Since vinylphosphine is almost a prolate symmetric top the rotational basis functions have the form

$$\begin{aligned} |J, K^+\rangle &= N[|J, K_a\rangle + (-1)^J|J, -K_a\rangle] \\ |J, K^-\rangle &= N[|J, K_a\rangle - (-1)^J|J, -K_a\rangle], \end{aligned} \tag{2}$$

where N is a normalization constant. Now the localized torsional–rotational basis functions can be defined for each symmetry species.

Case 1—A symmetry species:

$$\begin{aligned} |A(K \geqslant 0, J)\rangle &= |A\rangle_t|J, K^+\rangle \\ &= |B\rangle_t|J, K^-\rangle. \end{aligned} \tag{3}$$

Case 2—B symmetry species:

$$\begin{aligned} |B(K \geqslant 0, J)\rangle &= |A\rangle_t|J, K^-\rangle \\ &= |B\rangle_t|J, K^+\rangle. \end{aligned} \tag{4}$$

$|A\rangle_t$ and $|B\rangle_t$ are the torsional wavefunctions defined in Fig. 4. It should be noted that the number of localized torsional–rotational basis functions for each symmetry species is equal to the number of nonsuperimposable frameworks.

Now the Hamiltonian matrix can be built for A and B symmetry species and for four possible values of K_aK_c. The $\Delta K = 0, \pm2, \pm4$ matrix elements have the general form

$$\begin{aligned}
\langle \Gamma(K)|\hat{H}|\Gamma(K)\rangle &= h_1 + \gamma\{q_2K + \alpha(-1)^J[\delta_{K1}J(J+1)(f_1+\gamma g_2) \\
&\quad + \delta_{K2}(J-1)J(J+1)(J+2)(d_1+\gamma p_2)]\} \\
\langle \Gamma(K)|\hat{H}|\Gamma(K+2)\rangle &= [1+\alpha(-1)^J\delta_{K0}]^{1/2}\langle J,K|J_+^2|J,K+2\rangle(f_1+\gamma g_2) \\
\langle \Gamma(K)|\hat{H}|\Gamma(K+4)\rangle &= [1+\alpha(-1)^J\delta_{K0}]^{1/2}\langle J,K|J_+^4|J,K+4\rangle(d_1+\gamma p_2). \qquad (5)
\end{aligned}$$

The coefficients α and γ determine signs which depend on the symmetry and on the parity of K_aK_c and are given in Table VIII. Subscript 1 defines the torsional integrals $\langle A\|A\rangle_t$ or $\langle B\|B\rangle_t$, and subscript 2 the integrals $\langle A\|B\rangle_t$ or $\langle B\|A\rangle_t$. Each of the fitting parameters may be expressed as a polynomial in $J(J+1)$ and K^2,

$$\begin{aligned}
h_1 &= h_v + h_jJ(J+1) + h_kK^2 + h_{jj}[J(J+1)]^2 + h_{jk}J(J+1)K^2 + h_{kk}K^4 \\
&\quad + h_{jjj}[J(J+1)]^3 + h_{jjk}[J(J+1)]^2K^2 + h_{jkk}J(J+1)K^4 + h_{kkk}K^6 + \cdots \\
f_1 &= f_{1v} + f_{1j}J(J+1) + \tfrac{1}{2}f_{1K}[K^2+(K+2)^2] + \cdots \\
q_2 &= q_{2v} + q_{2j}J(J+1) + q_{2K}K^2 + \cdots. \qquad (6)
\end{aligned}$$

The rotational parameters in Eq. (6) can be easily compared to Watson's A representation of the asymmetric rotor Hamiltonian,

$$\begin{aligned}
h_j &= (B+C)/2, & h_{jk} &= -\Delta_{JK}, & f &= (B-C)/4 \\
h_k &= A-(B+C)/2, & h_{kk} &= -\Delta_K, & f_{1j} &= -\delta_J \qquad (7) \\
h_{jj} &= -\Delta_J, & h_{jjj} &= \Phi_J, & f_{1K} &= -\delta_K.
\end{aligned}$$

For the parameters responsible for the tunneling splittings, the notations of Eqs. (5) and (6) will be used.

The results of the fit to all observed rotational transitions in the ground vibrational state are given in Table IX. The standard deviation of the fit to 136 microwave and millimeter-wave transitions was 171 kHz. Sixty two of these transitions form doublets due to the torsional tunneling in vinylphosphine.

TABLE VIII

Coefficients in the Matrix Elements Defined in Eq. (5) and the Minimum Values of K

K_a	K_c	Symmetry	α	γ	J even	J odd
e	e	A	+	+	K≥0	K>0
e	e	B	-	-	K≥0	K>0
e	o	A	-	+	K>0	K≥0
e	o	B	+	-	K>0	K≥0
o	e	A	-	+	K>0	K>0
o	e	B	+	-	K>0	K>0
o	o	A	+	+	K>0	K>0
o	o	B	-	-	K>0	K>0

TABLE IX

Molecular Parameters for Vinylphosphine

A (MHz)	40484.173 (49)	1.000											
(B+C)/2 (MHz)	5216.1358 (5)	-0.009	1.000										
B-C (MHz)	483.8996 (11)	0.187	0.032	1.000									
Δ_J (kHz)	2.80046 (61)	0.078	0.351	0.500	1.000								
Δ_{JK} (kHz)	-23.9517 (94)	-0.062	0.460	-0.190	-0.313	1.000							
Δ_K (kHz)	447 (11)	0.913	-0.085	0.393	0.361	-0.260	1.000						
δ_J (kHz)	0.39540 (38)	0.001	-0.004	0.830	0.099	-0.086	0.079	1.000					
δ_K (kHz)	-10.04 (17)	0.273	-0.009	0.587	0.853	-0.312	0.584	0.111	1.000				
Φ_{KJ} (Hz)	-3.212 (44)	-0.031	0.399	-0.008	-0.015	0.903	-0.115	-0.051	0.015	1.000			
q_{2v} (MHz)	-10.330 (47)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000		
q_{2K} (MHz)	1.411 (11)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.708	1.000	
p_{2v} (Hz)	3.06 (16)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.143	0.673	1.000

The uncertainties shown in parentheses are in units of the last digits and are standard errors.

Table IX shows that the fit required an introduction of a high-order term in the Hamiltonian (1), $p(J_+^4 - J_-^4)$. With the lower-order term $g(J_+^2 - J_-^2)$ no reasonable fit of torsional splittings could be achieved. We assign this problem to the simplicity of our model: in the formalism no information has been included about the nature of the tunneling between two minima. The tunneling is treated rather as a "flip-flop" motion than as an internal rotation.

CONCLUSION

The determination of the dipole moment indicates unambiguously that the assigned spectrum is due to the gauche form. This is further confirmed by the structure determination and the observed internal rotation splittings. Searches for the spectrum of the syn form were unsuccessful. On the other hand ab initio calculations using different basis sets (from 3-21G* up to 6-311G(2*df*, *p*)) and levels of approximations (RHF, MP2, MP4) all predict that the syn form should be more stable.

ACKNOWLEDGMENTS

J.-C.L. and J.-L.A. thank the Dirección General de Investigación Científica y Técnica (Grants PB87-0898 and PB90-0345) for research support. P.D., M.L.G., J.-M.D., and J.D. thank the GDR CNRS Physico-Chimie des Molécules et Grains Interstellaires for support. The authors also acknowledge the exchange program Acción Integrada Hispano-Francesa (Grant 98B, 1992) for financial support. M.K. thanks the Commision of the European Communities for fellowship Grant PECO ERB3510PL920682.

RECEIVED: February 2, 1994

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